EFFECT OF NANO CLAY ON OILWELL CEMENT PROPERTIES FOR HIGH PRESSURE AND TEMPERATURE APPLICATIONS

BY

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Dedication

I dedicate my work to my parents and sisters who have been supporting to me in all my endeavors.

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LIST OF ABBREVIATIONS

μ_p	:	Plastic Viscosity
API	:	American Petroleum Institute
ASTM	:	American Standards for Testing and Measurement
Bc	:	Bearden Consistency Unit
BHCT	:	Bottomhole Circulating Temperature
BHP	:	Bottomhole Pressure
BHST	:	Bottomhole Static Temperature
BWOC	:	By Weight of Cement
BWOW	:	By Weight of Water
HPHT	:	High Pressure High Temperature
HSR	:	High Sulphate Resistant
ISO	:	International Organization for Standardization
MSR	:	Moderate Sulphate Resistant
MW	:	Mud Weight
NC	:	Nano Clay
NS	:	Nano Silica
OSR	:	Ordinary Sulphate Resistant
OWC	:	Oil Well Cement
PCF	:	Pound per Cubic Feet
PV	:	Plastic Viscosity
RPM	:	Rotation per Minute
SEM	:	Scanning Electron Microscope
TRB	:	Time to Reach Bottom

TVD	:	Total Vertical Depth
UCA	:	Ultrasonic Cement Analyzer
w/c	:	Water to Cement Ratio
WOC	:	Wait on Cement
XRD	:	X-ray Diffraction
YP	:	Yield Point

ABSTRACT

Full Name : Mobeen Murtaza

Thesis Title : Effect of Nano clay on oilwell cement properties for high pressure and temperature applications

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With the continued growth of petroleum demand, the oil and gas companies are searching in new or unexplored areas. The search is getting extreme in terms of depth, temperature and pressure. In deeper wells, high temperature and pressure and post cementing operations put extreme stresses on the cement sheath and affect the integrity of the cement. In such conditions, the design of cement slurry is very critical and it must possess properties which ensure the durability and long term integrity of cement sheath. To resolve this problem, many additives are being investigated and used in high pressure and temperature wells.

Recently, Nano Materials have demonstrated effectiveness across a wide variety of industries, from textiles and defense to aerospace and energy. They are now being used as commercially worthwhile solutions to technical challenges faced many industries. Having high surface area and small size, attracts them to petroleum industry. Their application in petroleum industry is progressing in a last few years.

The objective of this study is to evaluate the physical properties of Saudi cement class G with Nano clay addition and admixed with different additives such as fluid loss agent, retarder, expanding agent and friction reducing agent under high temperature and pressure conditions. Nano clay is added at different percentages to the cement slurry

mixture currently used for oil/gas well cementing in Saudi Arabia. Experimental investigations addresses different cement slurry properties such as thickening time, free water separation, rheological properties, compressive strength, density, porosity, permeability, and SEM and XRD analysis.

The best slurry design is selected on the basis of results of different percentages of Nano clay used in experiments. From the laboratory tests, it is investigated that addition of Nano clay improves the rheological and mechanical properties, reduces the free water contents, retards the thickening time, reduces the density, makes the strong micro-structure of cement and helps in designing the new cement system which sustains the high pressure and temperature conditions and gives good results. This new cement design can be prepared and implemented in the field without adverse effects.

ملخص الرسالة

الاسم الكامل: مبين مرتضى.

عنوان الرسالة: : تأثير الطفل النانوي على خواص اسمنت آبار النفط للتطبيقات عالية الضغط و الحراره

التخصص: هندسة البترول.

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مع الزيادة المتواصلة في الطلب على البترول، إتجهت الشركات للبحث في أعماق بعيدة ذات ضغط و حرارة عاليين، و في ظروف مماثلة، يتعرض التغليف الاسمنتي للآبار لإجهادات عالية ، و التي قد تؤثر سلباً على ترابط الاسمنت، ولذلك، فإن التصميم الأمثل للتركيبة الاسمنتيه أصبح بغاية الأهمية بحيث أنه يضمن إستمرارية و تماسك التغليف الإسمنتي لأطول فترة ممكنة، و للقيام بهذه المهمة، تم دراسة و إستخدام عدد مقدر من المواد المضافة في الآبار ذات الظروف المماثلة.

فى الآونة الأخيرة، أثبتت المواد الدقيقة الحجم، أو ما يعرف بالمواد النانوية، فعاليتها في مختلف المجالات، كالنسيج و الدفاع و الفضاء و الطاقة، و قد اصبحت الان مواد تجارية واسعة الإنتشار، لها القدرة على إيجاد الحلول للعديد من المصاعب التقنية، و في صناعة البترول، وجدت هذه المواد إنتشاراً نسبة لتميزها بكِبر مساحة السطح النوعية و صغر حجمها.

الهدف من هذه الدراسة هو تقييم الخواص الفيزيائية للاسمنت السعودي فئة جي بوجود المواد النانوية و مواد مضافة اخرى كالمواد المانعة لفقدان السوائل و المثبطات و المواد الموسعة، إضافة الى مانعات الإحتكاك، كل ذلك تحت درجات عالية من الحرارة و الضغط العالى. في هذه الدراسة، تم إضافة المواد النانوية بنسب مختلفة من التركيبة الكلية للخليط الاسمنتي المستخدم في آبار النفط و الغاز في المملكة العربية السعودية، و قد تمت دراسة مختلف الخواص المتعلقة بالخليط مخبرياً، كالخواص المتعلقة بزمن زيادة السماكة وفصل الماء الحر و الخواص الريولوجية المختلفة و قوة الضغط و الكثافة و النفازية و المسامية، إضافة الى بعض الإختبارات المجهرية كالمسح الإلكتروني و الحيود السيني.

من خلال النتائج المخبرية، تم إختيار افضل تركيبة للخليط الإسمنتي المحتوية على نسبة معينة من المواد النانوية. من خلال الإختبارات السابق ذكرها، وجد أن المواد النانوية المضافة لها المقدرة على تحسين الخواص الريولوجية و الميكانيكية، إضافة الى التقليل من المحتوى المائي والتثبيط من زيادة السماكة و تقليل الكثافة. كل هذه التحسينات تصب في تقوية التركيبة الدقيقة للإسمنت و تساعد على تصميم نظام إسمنتي جديد له القدرة على تحمل ظروف الضغط و الحرارة العاليين و قابل للتطبيق حقلياً بدون آثار عكسية.

CHAPTER 1

INTRODUCTION

1.1 Overview

Petroleum production and exploration has an utmost effect on the global economic structure. The world's oil consumption has been increasing day by day. It grew by 171% during the period from 1965 to 2008 *(*Naohiko Yahaba, 2010). Over the last two decades, the amount of oil consumption per year has exceeded the amount of newly found oil reserves. Therefore, with time, the possibility of an ultimate decrease in oil production is becoming a realistic scenario. However, the exact amount of undiscovered oil reserves is not well known. Hence, it is difficult to predict when the ultimate decrease in oil production will initiate and affect the overall global economy. The human culture and modern technological society are very much dependent on the earth’s oil and chemical feedstock. So with continued growth of petroleum demand, the oil and gas companies are exploring in new or unexplored areas. This search is getting extreme in terms of depth, temperature and pressure. In deeper wells, high temperature and pressure and post cementing operations put extreme stresses on the cement sheath and which could affect the integrity of the cement. In such conditions, the design of cement slurry is very critical and it must own properties which ensure the durability and long term integrity of cement sheath.

Improper oil and gas well design and well cementing can jeopardize oil production and high economic impact. Oil spills such as the recent Gulf of Mexico deep water horizon oil spill are some of the causes of oil loss from the global reserve. Besides economic losses, oil spills cause environmental disasters particularly in marine habitats because of toxic substances. The oil industry has been spending billions of dollars to invent more technologically advanced materials and equipment to improve oil extraction and to minimize loss of oil and gas. Nonetheless, the fact remains that it is virtually impossible to solve every new problem that may arise.

Cementing can be a bit complicated, depending on the region drilled and sections encountered. Therefore special attention has to be paid to cementing processes especially in high pressure high temperature (HPHT) wells. The secret to zonal isolation is the good bonding properties of the cement with the casing and the formation, but this can be affected by cement shrinking and stress changes induced by downhole variation of pressure and temperature. In HPHT formations, the wells are subjected to high temperature variations and these changes affect both the formation and the casings, causing expansion and contraction. This expansion and contracting of casing and plastic formation like salt causes cracks in the already set cement.

The setting of cement is by the reaction between water and cement. This process is called hydration and if it continuous, the pore pressure in the setting cement reduces with its pore spaces. The post-set cement consisting of minimal number of pore spaces when subjected to high loads in deep wells compression sets in and destroys the cement sheath by compaction of matrix porosity. This destruction of cement matrix can be said to be caused by mechanical failure or damage and they create cracks in the cement matrix. These cracks are a pathway for the migration of gas from the formation to the surface, thereby shortening the life of the well because the integrity of the cement has been compromised (Yetunde & Ogbonna, 2011).

Migration of gas through the cement has been an industry problem for many years. Some studies pointed out that approximately 80% of wells in Gulf of Mexico have gas transmitted to surface through cemented casing. For twelve months or more, after cement has set, it continues to hydrate and consequently develop in strength. After this time, it maintains the strength that it has attained except if it is attacked by agents of erosion. Cement will attain maximum strength after 15 days when exposed to temperatures exceeding 230^{o}F.

After these first two weeks, the strength slowly starts to decrease. This process of cement losing its strength is known as strength retrogression. Structural changes and loss of water are the agents of cement degradation. When cement is set, it contains a complex calcium silicate hydrate. At temperatures around 250^{o}F, this calcium silicate hydrate is converted to a weak porous structure (alpha-di calcium silicate) which causes strength retrogression. The rates at which these changes occur depend on temperature (Joel & Iseghohi, 2009).

The appropriate cement slurry design for well cementing is a function of various parameters, including the well bore geometry, casing hardware, formation integrity, drilling mud characteristics, presence of spacers and washers, and mixing conditions.

Over the last few decades, several types of new chemical admixtures such as retarders, viscosity modifying admixtures, accelerators, strength developers etc. have been introduced to optimize the properties of cement. Early age and hardened properties of cement systems are highly depended on the type and dosage of chemical admixtures used. The performance of chemical admixtures is strongly influenced by the chemical and physical properties of the cement. Most of the commercial chemical admixtures have been used with Ordinary Portland cement and for general purpose use. In order to deal with bottom hole conditions (wide range of pressure and temperature), a special class of cements called OWCs, specified by the American Petroleum Institute (API) (API Specification 10A, 2012) are usually used in the slurry composition. The interactions of OWC with different types of admixtures and the associated cement-admixture compatibility at high temperature are still largely unexplored.

Recently Nano materials are introduced in cement formulations to develop high early strength. Development of high performance materials for construction is possible by unleashing the potential of nanotechnology. Nano-materials (being smaller in size and higher in surface area) are used in several fields, including catalysis, polymers, electronics, and bio-medicals (Park & Road, 2004). Because of a higher surface area, these materials can also be used in oil well cementing to accelerate the cement hydration process (Heinold & Dillenbeck, 2002). Because of their wide range of applications, they can help enhancing final compressive strength and reducing fluid loss (Li & Wang, 2006; Campillo et al., 2007).

Few literature reports are available mentioning use of Nano-materials in the concrete industry. For example, Campillo et al., (2007) investigated the effect of Nano-alumina in belite cement. They found that addition of Nano-alumina enhances mechanical properties to some extent. Li et al., (2006) reported use of Nano silica or Nano iron oxide in cement mortar. Their results showed improvement in compressive and flexural strength compared to plain cement mortar. Patil & Deshpande, 2012; Senff et al., 2010; Ershadi et al., 2011 have reported that addition of nanomaterial such as Nano silica also results in a significant increase in the compressive strength of the cement mix and prevents strength retrogression at high temperature. Though Nano materials have shown their presence in other industries in recent years, their application in the oil and gas industry are still to be fully explored (Singh & Ahmed, 2010). They have potential to provide solutions to some of the upstream and downstream challenges the oil industry has faced for the past several years (Pourafshary et al., 2009).

Some of the examples of harnessing Nano materials in drilling fluids (Singh & Ahmed, 2010) suggest that it can bring revolutionary changes to additive development. To the best of the our knowledge, however, so far, no report describing actual use of Nano-materials with other additives to enhance properties of cement slurry systems for oilfield application has been documented.

The objective of this study is to demonstrate Nano materials help to improve the properties of cement. The main focus of research is on the effect of Nano clay material on the cement behavior in high pressure/temperature environment. A well located in the Middle East is selected to study the cement mixture design and then Nano clay material is added and the various effects are determined to select the optimum cement slurry design.

1.2 Need for This Research

The petroleum industry encounters several challenges in different areas and need more researches to yield in improvements and developments. One of the most difficult challenges associated with drilling and completion operations is assuring good cementing job in high temperature and pressure wells. Poor cementing jobs could result in serious consequences that may jeopardize the success of any oil and gas well.

Communications between zones, gas migration, undesired fluids entry, strength retrogression and stresses are examples of the serious consequences resulting from poor cementing jobs in HPHT wells. Companies and the academia are continuously conducting research projects to improve and develop new cements and chemical additives that enhance cementing oil and gas wells in hostile environments.

Successful applications of Nano Materials in drilling are likely to occur with synthetic nanoparticles, where size, shape and chemical interactions are carefully controlled to achieve the desired fluid properties and drilling performance. Nano Materials can lead to a better understanding and control of rock/fluid interactions and their effects on wellbore stability, fluid loss and formation damage, thereby leading to improved drilling efficiency (Zhang et al., 2009).

1.3 Problem Statement

Development of high performance materials for well construction is possible by investigating the potential of nanotechnology. Few literature reports are available mentioning use of Nano-materials in the petroleum industry. Their results showed improvement in compressive and flexural strength compared to plain cement mortar. Though nanotechnology has shown its presence in other industries in the past, its application in the oil and gas industry is yet to be fully explored (Singh & Ahmed, 2010). It has potential to provide solutions to some of the upstream and downstream challenges the industry has faced for the past several years (Pourafshary et al., 2009).

Since the cement slurry is pumped into the wellbore; issues such as thickening time, rheology, water loss, gas migration, development of slurry strength with time and cement shrinkage are as critical as high compressive strength developed after set. The research will investigate the effects of Nano clay on oil well cement slurry using Type-G cement which is used in oil and gas well cementing in Saudi Arabia.

1.4 Thesis Objectives

Cement slurry can be considered as a composite suspension of cement and supplementary cementitious materials in water, one or multiple chemical admixtures, fillers, etc. Oil well cement (OWC) slurries are pumped between the well bore and the steel casing inserted in the well to seal off all strata of the formation, except those that have oil so that gases and water do not contaminate the oil bearing strata. OWCs are sometimes pumped to depths in excess of 6000 m (20000 ft). At such depths, the temperature may rise up to 205°C (400°F). The cement slurry may also be subjected to very high pressures reaching over 200 MPa (30000 psi) (Joshi and Lohita, 1997) depending on the height and density of the column of material above it. Thus, oil/gas well cementing operations face additional challenges in contrast to common cementing work above ground. In addition to the high pressure and temperature, the OWC must be able to cope with weak or porous formations, corrosive fluids, etc.

A number of additives have been used to alter the chemical and physical properties of the OWC slurry as required for flow-ability and stability of the slurry and the long term performance of wells. The conventional admixtures which have been developed in countries with mild climates for cementing jobs above ground, may lead to inadequate results when exposed to high temperatures. Likewise, there is still a lack of information in the open literature regarding the effects of various chemical admixtures, such as new generation superplasticizers, on the properties of cement-based materials at high temperature. The present study attempts to develop a better understanding of the important mechanisms that controls the properties of OWC slurry subjected to severe conditions such as high temperature and pressure, and to investigate the performance of Nano clay admixture in controlling the properties of oil well cement slurries. This knowledge thus gained could ultimately allow the optimization of blended oil well cements, leading both to ecological and economic benefits.

Specifically the properties of OWC slurry using Nano clay will be studied;

a) Thickening time
b) Free water separation
c) Rheological properties
d) Compressive strength
e) Density
f) Porosity and permeability tests

g) XRD and SEM analysis

1.5 Thesis Organization

This thesis has been prepared according to the instructions specified by the Deanship of Graduate Studies of King Fahd University of Petroleum & Mineral. It has been divided into five chapters as follows;

Chapter 2: explains the literature review which covers the basics of cement, factors affecting cement design, additives and different cement properties. It discusses the previous researches conducted on the cement slurry development and different additives improvement over the years.

Chapter 3: explains the experimental program used for this research work. It presents the complete methodology of tests according to API Specifications conducted to measure the different properties of cement in high pressure and temperature conditions.

Chapter 4: presents the results and discussions of all experimental tests conducted to analyze the behavior of cement.

Chapter 5: concludes and highlights the major research outcomes with recommendations for future work.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Oil well cementing is the process of placing cement slurry in the annulus space between the well casing and the geological formations surrounding to the well bore. When a certain section of the depth of an oil or gas well has been drilled successfully, the drilling fluid cannot permanently prevent the well bore from collapsing. Therefore, oil well cementing was introduced in the late 1920s (Joshi and Lohita, 1997) with a number of objectives: (i) protecting oil producing zones from salt water flow, (ii) protecting the well casing from collapse under pressure, (iii) protecting well casings from corrosion, (iv) reducing the risk of ground water contamination by oil, gas or salt water, (v) bonding and supporting the casing (Labibzadeh, Zahabizadeh, & Khajehdezfuly, 2010), and (vi) providing zonal isolation of different subterranean formations in order to prevent exchange of gas or fluids among different geological formations (Jones, Carpenter & Co, 1991).

In addition to their exposure to hostile temperature and pressure conditions, oil well cements (OWCs) are often designed to cope with weak or porous formations, corrosive fluids, and over-pressured formations. The appropriate cement slurry design for well cementing is a function of various parameters, including the well bore geometry, casing hardware, formation integrity, drilling mud characteristics, presence of spacers and washers, and mixing conditions. The behavior of OWC slurries must be optimized to achieve effective well cementing operation. A strict control of the hardened cement mechanical properties and durability during the service life of the well are very important criteria, especially under such severe environments. Thus, a special class of cements called oil well cements (OWCs), has emerged and is specified by the American Petroleum Institute (API) (API Specification-10A, 2012). A number of additives have also been used to alter the chemical and physical properties of the OWC slurries as required for the flowability, stability of the slurry and to ensure long term performance of wells.

Extensive research has been conducted to improve the efficiency of oil well production by improving the physical and mechanical properties of OWC slurries. This chapter discusses the basic concepts involved in oil well cementing, the different types of OWCs, and their chemical and physical properties. An insight into the additives that can modify the behavior of the OWC systems and allow successful slurry placement between the casing and the formation, rapid compressive strength development, and adequate zonal isolation during the lifetime of the well is also provided.

2.2 Well Cement

A typical oil/gas well can be several thousand meters in depth, and of a few inches in diameter (Lafarge, 2009), and is usually constructed using a metal casing surrounded by a special cement slurry mix that seals the annulus space between the outer face of the tubing and the wall formation of the hole. Cement slurries are sometimes pumped to depths in excess of 6000 m (20000 ft). At these depths, hydrated Portland cement are subjected to temperatures in excess of 230°F, so it undergoes significant phase changes which result in substantial decrease in compressive strength of the cement slurry and increases its permeability at temperatures above 230^{o}F as a result of strength retrogression arising from the breakdown of its crystalline structure at such temperatures (Mehta and Monteiro, 2001). This would render the Portland cement ineffectual for high temperature applications.

After drilling the well to the desired depth, the drill pipe is removed and a longer string of casing is run into the well until it reaches its bottom. The circulatable completion fluids such as drilling mud must be removed and replaced with a hardened cement to ensure intimate contact and bonding of the cement with the casing and formation surfaces. Sufficient cement slurry is pumped down the inside of the casing and forced up the outside of the casing through the annular space between the casing and subterranean borehole wall (Detroit, 1983) using two-plug cementing method (Calvert, 2006; Oilfield Glossary, 2009). Pressure is applied above plugs by an aqueous displacement fluid to displace any remaining cement slurry (Detroit et al., 1983). Two types of cementing plug (top and bottom) are typically used on a cementing operation to allow the cement slurry to pass through the casing and to reduce the contamination of cement slurries by other fluids that remain inside the casing prior to pumping cement slurry (Oilfield Glossary, 2009).

Typically, the cement slurry is brought much higher than the production zones into the well bore to exclude undesirable fluids from the well bore so as to protect fresh water zones and corrosion of the casing (Calvert, 2006). After the cementing process, a curing time is allowed for the slurry to harden before beginning completion work or drilling to a deeper horizon. The set cement slurry forms a low permeability annulus and isolates the productive zone of the well from the rest of the formation.

2.3 Classification of Oil Well Cement

Oilwell cements are usually made from Portland cement clinker or from blended hydraulic cements. OWCs provide a base constituent in the slurry mix that is pumped into the interior metal casing of the well and forced back toward the surface from the base of the borehole filling the annulus (Powers et al., 1977, Detroit et al., 1981, Calvert, 2006). In the beginning, only one or two types of oil well cement were available. As oil/gas wells became deeper and subjected to more hostile environments, the more harsh performance criteria could not be satisfied by those cements. With the advent of the API Standardization Committee in 1937, improved OWCs were developed (Smith, 1987). The API Specifications for Materials and Testing for Well Cements (API Specification 10A, 2002) include requirements for eight classes of OWCs (classes A through H) as explained in **Table 2.1**. OWCs are classified into grades based upon their C_3A (Tricalcium Aluminate) content: Ordinary (O), Moderate Sulphate Resistant (MSR), and High Sulphate Resistant (HSR). Each class is applicable for a certain range of well depth, temperature, pressure and sulphate environments.

Class A, Class G and Class H are the three most commonly used oil well cements. Class A is used in milder, less demanding well conditions, while Class G and H cements are usually specified for deeper, hotter and higher pressure well conditions (Lafarge, 2009). Conventional types of Portland cement incorporating suitable additives have also been used. The chemical composition of cement is what distinguishes one type of oil well cement from another and determines the suitability of the cement for specific uses. The chemical composition of OWC is slightly different from that of regular Portland cement. OWCs usually have lower C_3A contents, are coarsely ground, may contain friction-reducing additives and special retarders such as starch, sugars, etc, in addition to or in place of gypsum (Popovics, 1992). The key features of commonly used OWCs are summarized in **Table 2.1**.

API Class G and H are by far the most commonly used OWCs today. The chemical composition of these two cements is similar. The basic difference is in their surface area.

Class H is coarser than Class G cement and thus has a lower water requirement. Cement that is ground too fine should not be used as oil well cement. Microfine cements and ultra-fine (blain surface> 9000 cm^2/gm) Portland cements cannot be used for primary cementing because it does not develop sufficient compressive strength to hold the casing in downhole condition and it does not generally have adequate sulphate resistance. However, microfine cement is a good option for oil well repairing since typical OWCs cannot be used because of their larger particle size and the subsequent difficulty to penetrate in extremely small cracks/channels (Kumar et al., 2002).

Table 2.1: Key features of API Oil Well Cement (API Specification 10A, 2002)

Cement Class	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**H**
w/c, % mass fraction of cement	46	46	56	38	38	38	44	38
Range of depth, m	0 to 1830	0 to 1830	0 to 1830	1830 to 3050	3050 to 4270	3051 to 4880	0 to 2440	0 to 2440
Availability	O* grade compatible with ASTM C 150, Type I Portland Cement	MSR** and HSR*** grades, Comparable with ASTM C 150, Type II	O*, MSR** and HSR*** grades, Comparable with ASTM C 150, Type III	MSR** and HSR*** grades	MSR** and HSR*** grades	MSR** and HSR*** grades	MSR** and HSR*** grades	MSR** and HSR*** grades
	Cost	Lower Cost	Lower Cost	More costly than ordinary porltland cement	More costly than ordinary porltland cement	More costly than ordinary porltland cement	--	--
Other features	Intended for use when special properties are not required	Intended for use when special properties are not required moderate or high sulphate resistance (2) lower C3A content than Class A	Intended for use when conditions require high early strength (2) The C3S content and surface area are relatively high	(1) Required under conditions of moderately high temperatur e and pressure (2) retarded cement and retardation is achieved by reducing C3S and C3A, and increasing the particle size of the cement grains	(1) Required under conditions of high temperatur e and pressure (2) retarded cement and retardation is achieved by reducing C3S and C3A, and increasing the particle size of the cement grains	(1) Required under conditions of extremely high temperatur e and pressure (2) retarded cement and retardation is achieved by reducing C3S and C3A, and increasing the particle size of the cement grains	(1) Basic well cement (2) Thickening times controllable with additives to prevent loss of circulations up to 250 F.	(1) Basic well cement (2) Surface area is coarser than Class G (3)Thickeni ng times controllable with additives to prevent loss of circulations up to 450 F.

On the other hand, American Society for Testing and Materials (ASTM) Specification C-150 develops eight types of Portland cement I-VIII with type I cement being the normal, general-purpose cement used for construction purposes. More than 92% of Portland cement used in the United States are type I and II (or Type I/II). Table **2.2** shows the ASTM cement classification and their use.

Table 2.2: ASTM cement Classification[67]

ASTM Cement Class	Use
I	General purpose cement, when there are no extenuating conditions. Similar to API class B
II	Aids in providing moderate resistance to sulfate attack. Similar to API class B
III	When a high early strength is required. Similar to API class C
IV	When a low heat of hydration is desired
V	When high sulfate resistance is required
IA	A type I cement containing an integral air- entraining agent
IIA	A type II cement containing an integral air- entraining agent
IIIA	A type III cement containing an integral air- entraining agent

2.4 Oil Well Cement Additives

Typical admixtures for OWC slurries can be categorized into eight groups: accelerators, retarders, extenders, weighting agents, dispersants, fluid-loss control agents, lost circulation control agents, and other special additives (antifoam agents, fibers, etc.). The OWC slurry may incorporate retarders or accelerators to control the setting behavior, weighting agents are light-weight systems to increase the density of the OWC slurry system, and extenders to lower the density of the cement system and increase its yield.

Similarly, different admixtures are used as dispersants or viscosifiers to control the viscosity of the slurry. For instance, fluid loss additives are used to control the loss of the aqueous phase of the OWC slurry to the geological formation and to maintain constant water to solid ratio in cement slurries, while lost circulation control agents are used to control the loss of the cement slurry to weak or regular formations. A detailed review of cement additives has been provided by Nelson et al. (1990 and 2006). In addition to chemical admixtures, a number of mineral additives such as fly ash, silica (α-quartz and condensed silica fume), diatomaceous earth, gilsonite, powdered coal (Nelson et al. 1990; Nelson et al., 2006), etc., have been used to alter certain properties of OWC slurries.

2.4.1 Accelerators

Accelerators shorten slurry's set time and allow the slurry to develop necessary early compressive strength in a practical time frame (Santra et al., 2012). Accelerators are used for shallow low temperature and pressure cement jobs where long thickening time is not necessary. The most common accelerators used are calcium chloride, sodium chloride and gypsum.

2.4.2 Retarders

Retarders delay slurry's set time. This delay allows the cement to be placed before hardening occurs. These additives counter the effects of increased temperature on cement slurry. The most commonly used retarders are calcium lignosulfate and borax.

2.4.3 Fluid Loss Agent

Excessive losses of water to the formation can prevent cement from hardening correctly. Fluid-loss control additives are used to reduce excessive losses of water to the formation. In addition, these additives:

- Increase viscosity
- Retard the set time
- Control free water in the slurry

The most common fluid loss agents used are the organic polymers and cellulose derivatives.

2.4.4 Extenders

Extenders lighten the density of the slurry for cementing across weak formations. Lighter slurry lowers the hydrostatic pressure and helps prevent formation damage. Mostly used extenders are fly ash and sodium silicate.

2.4.5 Anti-foaming Agent

Cement foaming is one of the problems associated with cement slurry while mixing. The entrapped air in the cement slurry could cause damage to the pumps in the field and also could cause incorrect density readings and consequently mixing incorrect cement slurry density.

Defoamers are used to minimize foaming problems and are normally used with every cement system. Defoamers are special additives developed by different companies and are available in powder or liquid for convenient use.

2.4.6 Free Water Control Additives

Free-water control additives tie up water in light weight or extended slurries. If this water were not controlled, the slurry properties would change as water was absorbed into the surrounding formations. This absorption affects slurry flow and placement. Aluminum chlorohydrate is mostly used to prevent free water.

2.4.7 Lost Circulation Control Agents

Controlling lost circulation is an important issue to be considered when cementing across highly permeable and vuggy formations as well as formations having natural or induced fractures.

Lost circulation might be controlled by reducing cement slurry density and by adding additives to act as a plugging bridge on the opening area of the high permeability zone or the fracture.

There are different types of lost circulation control agents, granular type (e.g. Gilsonite), flake type (e.g. cellophane), and fibrous agents (e.g. nylon)

2.4.8 Weighing Agent

Weighting materials can be used to increase the density of the cement or slag and help control formation pressures. Barite and hematite are most used weighing materials.

2.4.9 Dispersants

Dispersants reduce slurry viscosity, which is very important for placement and cohesion. Proper dispersion of a slurry results in:

- Enhanced early compressive strength
- Improved fluid-loss control
- Improved free-water control

Naphthalene sulfonate and broxin are commonly used dispersants.

2.4.10 Strength Retrogression Agents

Cement slurries that remain at temperatures above 200°F (94°C) exhibit a reduction of compressive strength over time. This phenomenon, called strength retrogression, can be minimized or prevented by adding another source of silica, such as silica flour or silica sand, to the slurry (Iverson et al., 2010).

2.5 Nano Materials

The oil products global demand is predicted to be increased by 50% in the next 20 years. However, the use of unconventional energy sources, such as nuclear and renewable energy will increase in the coming years, this increase will be comparatively small and the main role of the these unconventional energy sources will be to balance and complement, rather to swap the use of hydrocarbons. Therefore, meeting the World's growing energy demand will be a major challenge in the coming decades. Nanotechnology has the potential to fill the gap by providing technologies that are more proficient and environment friendly.

Nanotechnology refers to a field of applied science and technology which deals with the control of matter on the atomic and molecular scale, generally 100 nanometers or smaller, and the manufacturing of devices with critical dimensions that lie within that size range(Singh & Ahmed, 2010) . Specifically, advancements in nanotechnology have led to development of significantly enhanced enabling materials, tools, and devices with features and characteristics that cannot be matched by conventional technologies.

Nanoparticles provide exceptional properties because of their small size and high surface area per unit volume (see **Figure 2.1**). As a result, they have many useful applications including oil and gas exploration and production. The ability to measure and manipulate matter on the nanometer scale is making possible a new generation of materials with enhanced mechanical, optical, transport and magnetic properties. However, still much remains unknown about nanoparticles and why materials made from nanoparticles differ from those made using their larger counterparts. Nano materials act to be stronger and more reactive than non-Nano materials. It is also unclear why Nano fluids conduct heat so effectively. There is a common assumption that it may be related to the increased surface interface. Since, for a given volume of material, there are a greater number of particles as their size decreases, perhaps there is more surface area for the nanoparticles to conduct the heat. The transition from micro- to nanoparticles leads to changes in physical as well as chemical properties of a material. Two of the major factors are the increase in the ratio of the surface area to volume, and the size of the particle. High surface area-to-volume ratio, which increases as the particles get smaller, leads to an increasing dominance of the behavior of atoms on the surface area of particle over those in the interior of the particle (i.e., surface forces tend to dominate body forces); this affects the properties of the particles when they interact with other particles. As a result of the higher surface area of the nanoparticles, the interaction with other particles within the mixture is greater, potentially leading to increased strength of the material, heat resistance and other properties of the mixture. Nano materials properties depend highly on the shape, orientation and structure of nanoparticles.

Now a day, many Nano materials are being investigated in oilwell cementing for example Nano silica, Nano alumina, Carbon Nano tubes and Nano clay. Both Carbon Nano tubes and Nano clay have limited applications in oilwell cementing. Our research encircles the effects of Nano clay on oilwell cementing in HPHT applications.

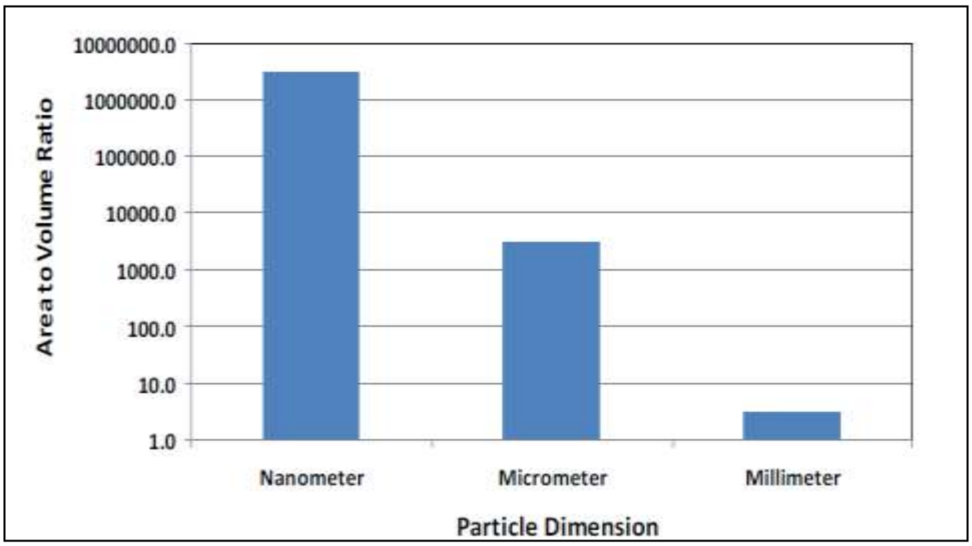

Figure 2.1: Area to volume ratio of different particles dimensions (Saidin, Sonny, & Nuruddin, 2008)

2.6 Cementing Design Process

The drilling and completion of a well is a capital project that goes into millions of dollars and hence, it is necessary to have inclusive design of the cement used for completion of a particular well to avoid remedial cement work which would put extra cost to the project. Cement design is usually formulated to a particular well according to prevailing downhole conditions which is followed by testing in the lab to determine if the design would be satisfactory.

Ravi and Xenakis, (2007) discussed a three step approach to cement design (see **Figure 2.2**). Step one includes a detailed engineering analysis. It requires classifying the nature of the formation- is it a hard or a loose formation? It requires ascertaining all forces that would come into play as the well is being produced- are there high temperatures, high pressures or both? Is it normally or abnormally pressured? Step one also covers stress analysis to determine if the cement sheath would sustain the series of cyclic loads it would encounter during its lifetime. The answers to step one questions can lead to step two which involves designing the cement slurry based on factors identified in step one. The properties of the cement like tensile strength, Young's modulus, Poisson's ratio, plasticity parameters, shrinkage/expansion during hydration, and post-cement slurry hydration are chosen so as to effectively match the effects of downhole conditions. Thereafter, laboratory investigations are conducted on the designed slurry.

The data from the laboratory tests and the analysis of step one are then analyzed together to evaluate performance. Step three involves best drilling and cementing practices such as centering of casing and effectively cleaning out hole of all mud so as not to undermine the performance of the designed slurry. It also comprises monitoring during the life of the well.

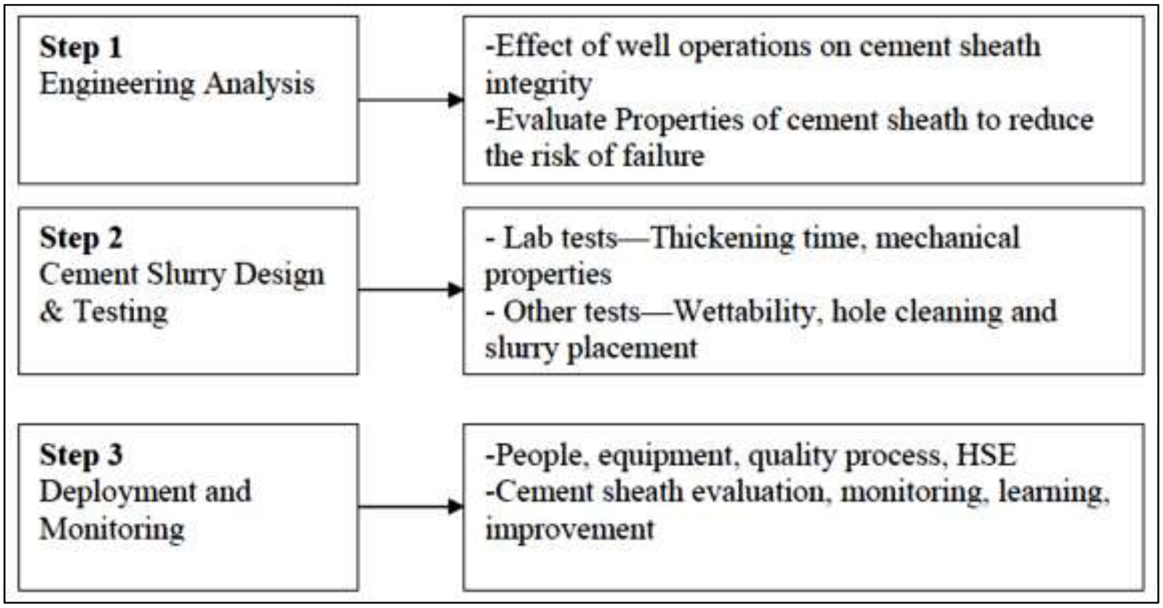

Figure 2.2: Three step process for cement design (Ravi and Xenakis, 2007)

2.7 Density of Oil well Cement Slurries

The density of neat cement slurry, i.e., mixture of water and cement, varies from 14.7 lb/gal to16.4 lb/gal depending on the API Class of the cement and the water/cement ratio (w/c). Higher density cement slurries may be required to control well fluids subjected to high bottomhole formation pressures. It is desirable to increase the density of OWC slurries to minimize the diffusion of heavy drilling muds. Usually bentonite and organic gums are used to prevent segregation of the heavy constituents from the cement slurry (Beaudoin et al., 1984). In other cases, lower density cements may be required to prevent lost circulation during well cementing. Density altering additives (weighting agents or extenders) are used to achieve specific density requirements. Weighting agents increase weight to the slurry to attain higher density, while extenders are low specific gravity materials that are used to reduce the slurry density and to increase slurry yield. For example, Barite, sand and micro sand have relatively high specific gravity and are finely divided solid materials used to increase the density of a drilling mud or OWC slurry. Barite ($BaSO_4$) is the most commonly available weighting agent in oil/ gas well cementing, with a minimum specific gravity of 35 lb/gal (Oilfield Glossary, 2009). Hematite, calcium carbonate, siderite, manganese tetraoxide (Michaux & Nelson, 2006) sand and micro sand (Halliburton, 2009) are other types of weighting agents, but only barite and hematite have related API/ISO standards (Oilfield Glossary, 2009).

In the past decade, the Nano particles proved promising applications in oil industry which bring solutions to many challenges. (Ershadi et al., 2011) have reported that addition of Nano material such as Nano silica helps in designing light weight cement slurry by reducing density of the cement mix.

2.8 Porosity and Permeability of OWC Slurries

The volume and size distribution of pores affect not only the mechanical strength of cement based materials, but also its durability. The porosity and pore size distribution of a hardened OWC slurry depends on a number of factors such as the w/c ratio, degree of hydration, type of cement, mixing conditions, chemical admixtures and mineral additives, etc. High temperature has a drastic effect on the pore structure and compressive strength of cement based materials. The total porosity is more than doubled when the curing or casting temperature increases from 20°C to 1000°C (Komonen &Penttala, 2003).

Justnes et al., (1995) studied the change in porosity and pore size distribution as a function of time during the setting period for a plain API Class G cement with a w/c ratio = 0.5 at both 20°C and 60°C. It was found that although there was enough liquid volume to allow gas intrusion and percolation to occur, the pore entries were so small (1.0-1.6 μm in diameter) that gas could enter only as small bubbles or when dissolved without disruption of the matrix. Polymeric latexes were found to improve the ability of the hardened OWC to prevent migration of reservoir fluids from one zone to another by decreasing permeability and preventing gas migration through the set slurry in the semi-solid state(Nakayama ad Beaudoin, 1987). It was reported that the increased amount of fiber in latex modified cement led to an increase in the porosity and permeability of the hydrated OWC. Lightweight cement systems cured for 7 days at 185°F and 3000 psi exhibited lower permeability and porosity (Moulin et al., 1997). In the past decade, the novel properties of Nano particles attracted the enormous attention(Park & Road, 2004). They proved as the best way to reduce the permeability and porosity of concrete(G. Li, 2004; Shih et al., 2006). Later their applications in oil industry bring solutions to many challenges especially in high temperature and pressure conditions. Ershadi et al., 2011 have reported that addition of Nano material such as Nano silica results in a significant decrease in the permeability and porosity of the cement mix and prevents gas migration at high temperature.

2.9 Mechanical Properties of OWC

The compressive strength properties determine the integrity of cement and its ability to bear long term imposed stresses (Bourgoyne Adam, 1986).

Cement sheath is subjected to deterioration under extreme conditions. The extreme temperature cycling of the well bore results in severe mechanical damage and ultimate failure of the cement sheath, potentially leading to micro-cracks (Saidin et al., 2008) The rate of deterioration is generally intensified at high temperature and pressure such as in the case of oil and gas deep wells. A strict control of cement reactivity and mechanical properties during the life cycle of the well is thus very essential. The oil well cement system should meet a wide range of short-term criteria such as free water, thickening time, filtrate loss, development of strength, shrinkage, etc., in addition to various long-term requirements including resistance to chemical attack, thermal stability and mechanical integrity of the cement sheath (Ravi et al., 2002). The mechanical properties of hardened OWC slurry are affected by a number of factors and depend on the chemical composition of its constituents, temperature, curing regime etc.

Jones et al., (1991) presented a combined (latex and thixotropic) cementing system that improved cement bonding and zonal isolation in wells having bottom hole static temperature below 175 °F. Laboratory studies and case histories indicated that adopting this system would yield in better primary and remedial cementing through gas migration prevention, high degree of zonal isolation, filtrate loss reduction with rapid compressive strength gain, and minimal waiting on cement.

Golapudi et al., (1993) and Shih et al., (2006) investigated the effects of fly ash and silica fume on the properties of neat oil well cement of class G and Portland land composites respectively. The use of fly ash and silica fume increased the amount of water reducer and improved the compressive strength of cement but they could be used in low formation pressure reservoirs (Golapudi et al., 1993) .

The compressive strength decreases with the addition of MgO, while the shear bond strength increases with the addition of MgO (Buntoro et al., 2000). The addition of 3 to 5% by weight of cement (BWOC) of neat MgO as an expanding additive provides an excellent shear bond and acceptable compressive strength in geothermal and oil well cements at high temperatures of up to 250°C (Buntoro et al., 2001; Saidin et al., 2008). For cement slurry composed of 35% silica flour and 3% MgO (BWOC), 3 days of curing result in higher shear bond strength and compressive strength.

Micro-silica (also called condensed silica fume), because of its high degree of pozzolanic activity, has allowed the introduction of low-density cement systems with higher rate of compressive strength development (Carathers and Crook, 1987). As the exploration of deep wells increased, the use of silica flour in the range of 30%-40% has generally maximized to Portland cement to combat strength retrogression in cement sheath and to reduce permeability at high temperature (Iverson et al., 2010; Jupe et al., 2011).

Last few years, the Nano particles got momentum in petroleum industry because of wide range of applications as they help developing high early strength and controlling fluid loss(Li et al., 2006; Campillo et al., 2007). High performance materials for construction can be developed by investigating the potential of Nano materials. Nano-materials (being smaller in size and higher in surface area) are used in several fields, including catalysis, polymers, electronics, and bio-medicals (Park & Road, 2004). Because of a higher surface area, these materials can also be used in oil well cementing to accelerate the cement hydration process (Heinold et al., 2002). Few literature reports are available mentioning use of Nano materials in the concrete industry. For example, Campillo et al., (2007) investigated the effect of Nano alumina in belite cement. They found that addition of Nano alumina enhances mechanical properties to some extent. Li et al., (2006) reported use of Nano silica or Nano iron oxide in cement mortar. Their results showed improvement in compressive and flexural strength compared to plain cement mortar. Patil

& Deshpande (2012), Senff et al., (2009), Ershadi et al., (2011) and Morsy et al., (2012) have reported that addition of nanomaterial such as Nano silica and Nano clay also results in a significant increase in the compressive strength of the cement mix and prevents strength retrogression at high temperature.

2.10 Rheology of OWC Slurries

The rheological properties of an oil well cement (OWC) slurry defines the value of the final product and assists predicting its end use performance and physical properties during and after processing. Rheological measurements can determine the flow properties of the cement slurry such as its plastic viscosity (μ_p), yield point, frictional properties, gel strength, etc. Rheology studies the flow of fluids and deformation of solids under stress and strain. In shear flows, imaginary parallel layers of liquid move over or past each other in response to a shear stress to produce a velocity gradient, referred to as the shear rate, which is equivalent to the rate of increase of shear strain (Douglas et al., 1995).

The rheological properties of OWC slurries are important in assuring that the slurries can be mixed at the surface and pumped into the well with minimum pressure drop. The rheological properties of the cement slurry also play a critical role in mud removal. A proper flow regime must be sustained for thorough removal of the mud from the well bore (Nelson, 1979). The flow regime of a cement paste or slurry can change with time, temperature, pretreatment, application of shear, type of application, type of dispersion, physical and chemical characteristics of solid and liquid ingredients, the addition of special surface-active agents, and the extent of grinding and mixing.

The rheological behavior of the cement slurry also depends on a number of factors including the water-cement ratio, size and shape of cement grains, chemical composition of the cement and the relative distribution of its components at the surface of cement grains, presence of additives, mixing and testing procedures, etc. (Guillot, 1990). The concentration and shape of solid particles has a significant effect on the rheological properties of OWC slurry. The yield stress and plastic viscosity of cement paste usually increase as the cement becomes finer (Berg, 1979) and/or as the particle concentration increases (Barnes, 1993).

The rheology of OWC slurries is generally more complicated than that of conventional cement paste. In order to deal with with bottomhole conditions (wide range of pressure and temperature), a number of additives are usually used in the OWC slurries and the slurry shows different characteristics depending on the combination of admixture used. Sulfonates (polynapthalene sulfonate, lignosulfonates) are the most commonly used cement dispersants. Lignosulfonates should not be used at lower temperature because of its retardation effect (B. Nelson et al., 1990).

It has been observed that the flow of OWC slurries follows the Bingham plastic model almost perfectly (Guillot, 1990). It was found that the viscosity of a Class G cement slurry decreases with the addition of a lignosulfonate dispersant (Guillot, 1990). The yield value of the cement slurry decreased with increasing concentration of the dispersant (Michaux and Defosse, 1986). Glycerin acts as a slurry viscosifier and it was found that the associated increase in viscosity at lower shear rates is significantly lower than that at higher shear rates (P.Saasen et al., 1991). Moreover, the incorporation of sub-micron size polymer latex (Nakayama, 1987; Su et al., 1991) and replacement of cement by polymer powder (Chougnet et al., 2006) can lead to a significant reduction in the OWC slurry viscosity, and therefore can improve mixability and pumpability. Rheological and hydraulic properties of foams (complex mixtures of gasses and liquids or slurries) are largely influenced by foam quality, liquid-phase viscosity, temperature, and pressure.

Rheological properties can be improved by incorporating the Nano Particles in cement (Ershadi et al., 2011). Nano particles increase the viscosity and yield point of slurry which results improving the performance of slurry (Santra et al., 2012). The effect of Nano silica on the rheological properties of the fresh cement mixture can be used to the benefit of cement-based materials in that it improves the consistency of certain types of concrete (i.e., self-compacting concrete) and reduces the probability of bleeding and segregation (Jalal et al., 2012; Leemann & Winnefeld, 2007).

2.11 Setting and Thickening Time of OWC Slurries

Oilwell cement slurries are subjected to a wide range of pressure and temperature, which has major influence on the time required for their setting and hardening. The setting time is an important requirement in oil-well cementing. A premature setting can have disastrous consequences due to loss of circulation in the well, whereas too long setting times can cause financial losses due to high WOC, in addition to possible segregation of the slurry or contamination by fluids. OWC slurries must also harden rapidly after setting. A slow setting behavior can be achieved by adjusting the composition of the cement and or by adding retarders. Constituents of the cement slurry and their percentage can affect the hardening time. For example, the setting time can usually be increased by reducing the proportion of tricalcium aluminate (C_3A). Setting times of up to 4 hours at a temperature of 93^{o}C (200°F) and 6 hours at a temperature of 21^{o}C (70°F) can be achieved with a Portland cement with no C_3A (Ramachandran, 1984). Retarders can increase setting times up to 6½ hours at a temperature of up to 104^{o}C (220°F) (Ramachandran, 1984). For oil well construction, it is generally desirable to maintain the setting time of the cement slurry fairly constant over the temperature range of 60^{o}C (140°F) to 104^{o}C (220°F). Accurate control of the thickening time, i.e. the time after initial mixing at which the cement can no longer be pumped, is crucial in the oil well cementing process. It is important to simulate the well conditions (temperature, pressure, etc.) as precisely as possible in determining the thickening time. There are some other factors that affect the pumpability of the slurry, but are very difficult to simulate during determining the thickening time of the slurry, such as fluid contamination, fluid loss to formation, unforeseen temperature variations, unplanned shutdowns in pumping, etc. (Hallibutton, 2009).

The thickening time is usually controlled by using retarders. The addition of carbohydrates such as sucrose can significantly extend the thickening time or even prevent setting completely (Bentz et al., 1994). But these are not commonly used in well cementing because of the sensitivity of the degree of retardation to small variations in concentration (Nelson et al., 1990; Bermudez, 2007). It was found that the sugar acts as a retarder of cement slurries when added in small concentrations and as an accelerator when added in high concentration (Bermudez, 2007). Lignosulfonates and hydroxycarboxylic acids are retarders that are believed to perform well for OWCs with low C3A contents (Nelson et al., 1990). The mechanism by which these chemicals and others act as retarders is not well understood and is still a matter of controversy, but it is known that retarders bind to calcium ions (Taylor, 1997) and are able to inhibit the growth of ettringite crystals (Coveney and Humphries, 1996).

A multiphase, multicomponent model for the hydration of OWC in the presence of retarders was proposed by (Billingham et al., 2005). It was found that the chemical actions of the retarders contribute to slowing the initial rate of hydration reactions and the sudden crystallization of ettringite. Other retarders used in well cementing include cellulose derivatives, organo-phosphonates and inorganic compounds such as acids and salts of boric, phosphoric, hydrofluoric, and chromic, zinc oxide (ZnO) and Borax ($Na_2B_4O7.10H_2O$), sodium chloride (concentrations greater than 20% BWOW) (Nelson et al., 1990; Nelson et al., 2006). The thickening time of OWC slurries was also found to increase with the addition of polyvinyl alcohol (PVA) latex (Lu et al., 2005; Ding et al., 2001). Thickening time was found to be almost independent of temperature when the Engineered Cement Set Control Additive (ECSA) additive was used in the slurry, and the slurry allowed efficient and reliable cementing of long cement columns with a large temperature differential between the top and the bottom (Moradi et al., 2006).

Unlike retarders, $CaCl_2$, NaCl, and sodium silicates are used to shorten the setting time and offset the set delay caused by other additives such as dispersants and fluid loss control additives. The accelerating effect of such chemicals depends on their chemical nature, concentration, curing temperature and other constituents of the cement slurry. Salts of carbonates, aluminates, nitrates, sulphates, thiosulphates, as well as alkaline bases such as NaOH, KOH, and NH_4OH accelerate the setting time (Nelson et al., 1990; Nelson et al., 2006). Glycerin contents of 26% by volume or less were also found to accelerate the hydration process of Class G OWC slurries (Saasen, 1991).

A recent contribution has found that Nano materials accelerates the hydration of cement and helps in reducing the wait on cement in low temperature wells (Santra et al., 2012). Materials such Nano silica and Nano-C-S-H (calcium silicate hydrate), are known to be good accelerators for cement hydration (A. Martinelli et al., 2004; Santra et al., 2012).

2.12 Hydration of Cement Slurries

Portland cement consists of five major compounds and a few minor compounds. The composition of a typical Portland cement is listed by weight percentage in **Table 2.3**.

Table 2.3: Composition of Portland cement with chemical composition and weight percent (Roij, Egyed & Lips, 2012)

Cement Compound	**Symbols**	**Weight Percentage**	**Chemical Formula**
Tricalcium silicate	C_3S	50	$3CaO.SiO_2$
Dicalcium silicate	C_2S	25	$2CaO.SiO_2$
Tricalcium aluminate	C_3A	10	$3CaO.Al_2O_3$
Tetracalcium aluminoferrite	C_4AF	10	$4CaO.Al_2O_3.Fe_2O_3$
Gypsum	-	5	$CaSO_4.2H_2O$

When water is added to cement, each of the compounds undergoes hydration and contributes to the final product. Only the calcium silicates contribute to strength. Tri-calcium silicate is responsible for most of the early strength during first 7 days. Di-calcium silicate, which reacts more slowly, contributes only to the strength at later times. The equation for the hydration of tricalcium silicate is given by:

Tricalcium Silicate + Water ---> Calcium Silicate Hydrate + Calcium Hydroxide + Heat

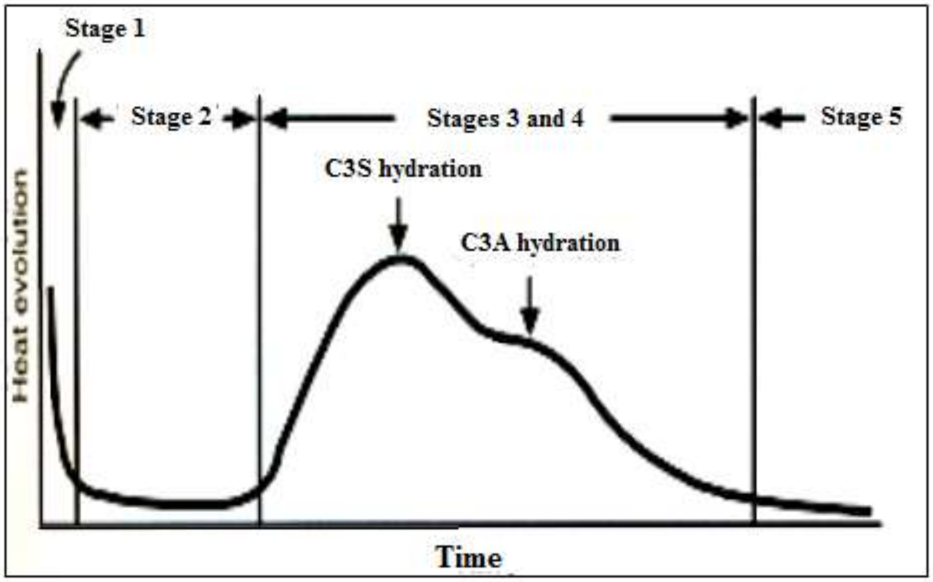

Figure 2.3: Schematic representation of hydration of Portland cement (Michaux & Nelson, 1990)

Upon the addition of water, tricalcium silicate rapidly reacts to release calcium ions, hydroxide ions, and a large amount of heat. The pH quickly rises over 12 because of the release of alkaline hydroxide (OH^-) ions. This initial hydrolysis slows down quickly with a corresponding decrease in heat (see **Figure 2.3**).

The reaction slowly continues to produce calcium and hydroxide ions until the system becomes saturated. Once this occurs, the calcium hydroxide starts to crystallize. Simultaneously, calcium silicate hydrate begins to form. Ions precipitate out of solution accelerating the reaction of Tricalcium silicate to calcium and hydroxide ions. The evolution of heat is then dramatically increased again. The formation of the calcium hydroxide and calcium silicate hydrate crystals provide "seeds" upon which more calcium silicate hydrate can form. The calcium silicate hydrate crystals grow thicker which makes it more difficult for water molecules to reach the anhydrate

Tricalcium silicate. The speed of the reaction is controlled by the rate at which water molecules diffuse through the calcium silicate hydrate coating. This coating thickens over time causing the production of calcium silicate hydrate to become slower and slower.

The setting and hardening of OWC slurry are the result of a series of simultaneous and consecutive reactions between water and the constituents of the cement. Vlachou and Piau (1997) studied the microstructural and chemical evolution of Class G OWC slurry from the first minutes after mixing the cement powder with water until the beginning of setting. Based on scanning electron microscopy (SEM) and X-ray Diffraction (XRD), it was concluded that the form and structure of the hydration products were a function of experimental conditions, such as hydration time since mixing, stirring conditions (Vlachou and Piau, 1997), temperature (Justness et al., 1995), chemical composition of cement and additive used (Vidick, 1989) etc. The slurry hydrated under continuous stirring showed constant viscosity and adequate fluidity over several hours. The formation of small spheres of hydration particles of the aluminate phases had no influence on the flow curve probably because these particles created no bonds between them and they moved freely into the inter-particle spaces.

Subsequently, the slurry thickened rapidly with the multiplication of hydrated crystals and the start of setting processes (Vlachou and Piau, 1997). On the other hand, slurries hydrated at rest showed a much more increase of viscosity during the first hours, after which the evolution process slowed down (Vlachou and Piau, 1997). It was reported that in case of slurries hydrated at rest, an over-saturation of ions in the grain neighborhood leads to the formation of aluminate hydration crystals of colloidal size (Vlachou and Piau, 1997). These crystal cover the surface of the grains and the hydration reaction eventually slows down. On the other hand, ions dispersed all over the sample volume and dissolution continues until saturation in case of slurries hydrated under stirring. The chemical composition of cement and additives used can affect the evolution of the chemical composition of the liquid phase of the cement paste (Michaux & Nelson, 1989). X-ray diffraction and scanning electron microscopy showed that a neat cement slurry changes from CSH(II), C_2SH_2, $C_3S_2H_3$ to dicalcium silicate hydrate (C_2SH) when the temperature exceeds 110°C and the microstructure of hardened slurry changes from a three-dimensional fiber network to a blank block or mass block for different curing temperature conditions (Zhang et al., 2008)

On the other hand, the major products of cement slurry with silica sands changes into $C_5S_6H_5$, C_6S_6H (> 150°C), $C_5S_5A_{0.5}H_{5.5}$, $C_{3.2}S_2H_{0.8}$ or other kinds of calcium silicate hydrate at high curing temperatures and the microstructures are transformed into a fiber network, rough frame network, short-parallel-needle fiber or mass block structure (Zhang et al., 2008). Different cements show different sensitivity to additives, thus exhibiting different behaviors when mixed with the same additives (Vidick et al., 1989; Jupe et al., 2007). According to Justnes et al. (1995) only about 10% hydration is necessary for a plain API class G cement slurry with w/c = 0.5 to retain its shape at atmospheric pressure. Even though, changes in the hydration of C_3S with pumping time of cement slurries could not be correlated, it was found that the largest changes in pumping time as a function of temperature occurred in a temperature interval where ettringite/monosulphate decomposes and crystalline hydro garnet started to be formed (Jupe, 2005).

When the Nano-based product is used as additive, moisture remains necessary for hydration and hardening. The five major compounds of the hydration process of cement still remain the most important hydration products but the minor products of hydration probably change. Furthermore, the rate at which important hydration reactions occur and the relative distribution of hydration products changes as a result of the addition of the active Nano material. In addition, the crystallization of calcium hydroxide occurs at different rates and the reduction of heat generation from the hydration reactions takes place as well. More crystals form during these reactions and the relevant crystalline matrix is much more extensive.

When adding the Nano materials, the water changes chemically in sphere, electrical load, surface tension and reaches a chemical/physical equilibrium in the matrix. This complex process depends on the type and mass of materials involved in the cement slurries. Similar to the chemical processes physical aspects are part of the equilibrium process in the matrix when the amount of water, trapped as free water is reduced and the crystals grow into the empty void space. This makes the product less permeable to water and more resistant to all types of attack that are either water dependent or water influenced. A larger fraction of water is converted into crystalline water than is the case with the chemical reactions in the absence of the Nano material. The reduced porosity and increased crystalline structural matrix increases compressive, flexural and breaking strength of the product and change the relative ratios between these forces. Water continues to play a critical role, particularly the amount used in the initial phase of the hardening process. With conventional oilwell slurries, the strength of the product increases when less water is used. The hydration reaction with added Nano material consumes a different amount of water, it is now also possible to use salt water and achieve satisfying results.

The porosity is still determined by the water to cement ratio but is affected to a lesser extent as a result of the increased rate and extent of the crystallization process. The extended crystallization process changes significantly with the active Nano material. The active Nano material causes a chemical physical equilibrium in the oilwell cement slurry based on synergy between water percentage and API Class G oil well cement. The chemical reaction takes place based on water as a catalyst. As a result strong hydrogen bonds form which significantly contribute to the bonding forces. The binding mechanism changes from “glue” to “wrapping”. The cement slurry produces a crystalline structure that is able to partially block capillary pores. Because of this fibre- like structure it become flexible and prevents micro cracking to occur (De La Roij et. al, 2010).

CHAPTER 3

EXPERIMENTAL PROGRAM

Cement lab testing is a main way to evaluate and develop different properties of cement system and to simulate the actual behavior of the cement in high pressure and temperature down hole environment.

The experimental program planned for this study is implemented according to the American petroleum institute (API) (API Specifications-10A, 2012) procedures and consists of several cement tests and each addresses to certain cement property. The properties of cement included in this research are:

a. Thickening time
b. Density
c. Rheology
d. Free water separation
e. Compressive strength test
    - Compressive strength by “Crushing” method
    - Compressive strength by “Sonic” method
f. Microstructural analysis
    - XRD
    - SEM

3.1 Well Specifications

A cement design of typical well of Saudi Arabia has been selected to test the behavior of Nano clay on cement design performance. The specifications of well are given in **Table3.1**.

Table3.1: Well specifications

Well Parameters	Values
Depth of well (TVD)	14000ft
Bottom hole circulating temperature (BHCT)	228^{o}F
Bottom hole static temperature (BHST)	290^{o}F
Time to reach bottom (TRB)	49min.
Surface pump pressure	1050psi
Mud weight(MW)	85PCF
Bottom hole pressure(BHP)	8265psi

3.2 Cement Slurry Design

The particular well has a special cement system design since the well is deep with high pressure and temperature conditions. The selected cement system consists of different materials in which each material contributes and adds chemical and physical property to make the cementing job successful.

The **Table 3.2** explains the cement slurry design of particular well without addition of Nano clay.

Table 3.2: Cement slurry design without Nano clay

Properties	Values
Slurry Density(Approx.), PCF	125
Water Cement Ratio	0.44
Slurry Yield	1.367
Thickening Time	4 - 5 hours
Class G cement powder + 35% silica flour + 1% expanding agent + 0.8% Dispersant + 0.2% Fluid loss control agent + 0.5% Fluid loss control agent + 1% Retarder + 0.25gm Defoamer	

A series of tests will be conducted on the slurry design without Nano clay according to the experimental program results in the base slurry design which will be used as a reference. After the base cement slurry design, the Nano clay material will be incorporated in the above cement slurry design in different percentages by weight of cement (1%, 2%, 3% &4) as **Table 3.3** explains the cement slurry design in the presence of Nano clay.

Table 3.3: Cement slurry design with Nano clay

Properties	Values
Slurry Density(Approx.), PCF	Unknown
Water cement Ratio	0.44
Slurry Yield	Unknown
Thickening Time	Unknown
Class G cement powder + 35% silica flour + X% Nano clay + 1% expanding agent + 0.8% Dispersant + 0.2% Fluid loss control agent + 0.5% Fluid loss control agent + 1% Retarder + 0.25gm Defoamer	

Where, X represents the Nano clay percentages (1%, 2%, 3% &4%) BWOC.

3.3 Materials

Cement slurries used in this study are prepared using high sulfate-resistant API Class G oil well cement with a specific gravity of 3.14. The chemical properties of simple class G cement are summarized in **Table 3.4**. All the cement slurries have been prepared using Tap water. A number of conventional chemical admixtures from Halliburton have been used as the **Table 3.5** explains the functions and concentrations of additives used in research. **Figure 3.1** shows the additives along with new-generation admixture, Nano clay, used in this research work.

Table 3.4: Chemical composition of Class G cement

Chemical Component (%)	
Silica (SiO_2)	21.6
Alumina (Al_2O_3)	3.3
Iron Oxide (Fe_2O3)	4.9
Calcium Oxide, Total (TCaO)	64.2
Magnesium Oxide (MgO)	1.1
Sulphur Trioxide (SO_3)	2.2
Loss on Ignition	0.6
Insoluble Residue	0.3
Equivalent Alkali (as Na_2O)	0.41
C_3A	<1
C_3S	62
C_2S	15
C_4AF+2C_3A	16

Table 3.5: Commercialized additives with their functions and percentages

Additives	**Functions**	**Concentration (%BWOC)**
SSA-1	Strength stabilizing agent	35
MBHT	Extender	1
HR-12	Retarder	1
CFR-3	Friction reducer	0.4
Halad-344	Fluid loss controlling agent	0.2
Halad-413	Fluid loss controlling agent	0.5
DA-3000	Anti-foaming agent	0.25/10bbl

Figure 3.1 Additives used in experiments

3.3.1 Nano Clay Properties

There is, as yet, no uniform nomenclature for clay and clay material. In General, clay imply a natural, earthy, fine grained material which develops plasticity when is mixed with a limited amount of water. As a particle-size term, the clay fraction is that size fraction composed of the smallest particles. Nano Clay is composed essentially of silica, alumina and water and lesser quantities of iron, magnesium, sodium and potassium as composition is given in **Table 3.6**. From the composition of Nano clay, it can be evaluated that the Nano clay is formed from Chlorite clay mineral as Fe and Mg elements exit in the composition. Chlorite clay is non expendable clay type as the central cation in octahedral sheets is Fe or Mg (see **Figure 3.3**).

Table 3.6: Elements concentrations in Nano clay

Elements	**Concentration (%)**
Si	31.82
Al	11.82
Fe	5.84
Mg	1.04
Ca	0.42
Cl	0.58
Ti	0.12
S	0.04
K	0.04
Cr	0.02
Zn	0.02
O	48.89

From the **Figure 3.2**, it is evident that Nano-clay is a layered material with a thickness in the order of 10 A° and with a width extending up to 1000 nm. One gram of powdered material can have billions of Nano particles with a surface area of many square meters (Uddin, 2008). The particle size is one of the most important aspects of Nano clay and the knowledge of knowing not only the average size but also understanding how the sizes are distributed would be of great importance in Nano compositing. The **Table 3.6** explains the elements concentration of Nano clay material. Nano-clay (**Figure 3.4**) increases stiffness, strength and heat resistance but decreases moisture absorption, flammability and permeability to gas and water. This in turn can result in significant usage in oil cement for improving its properties.

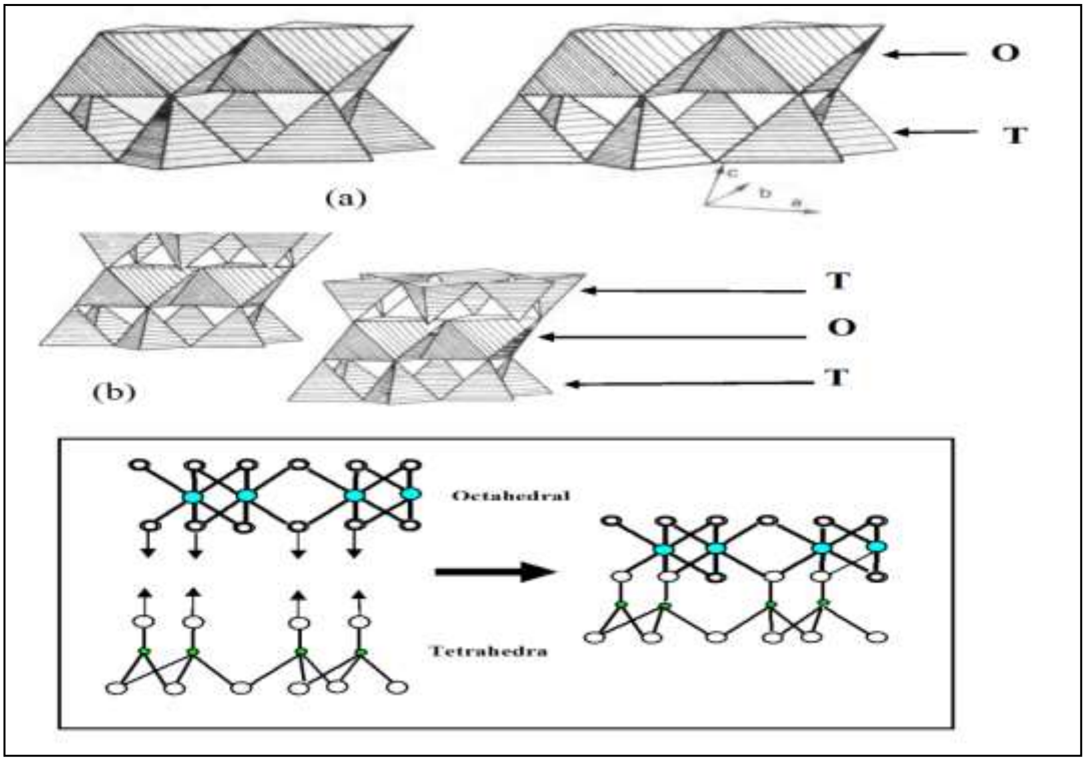

Figure 3.2: Structure of clay

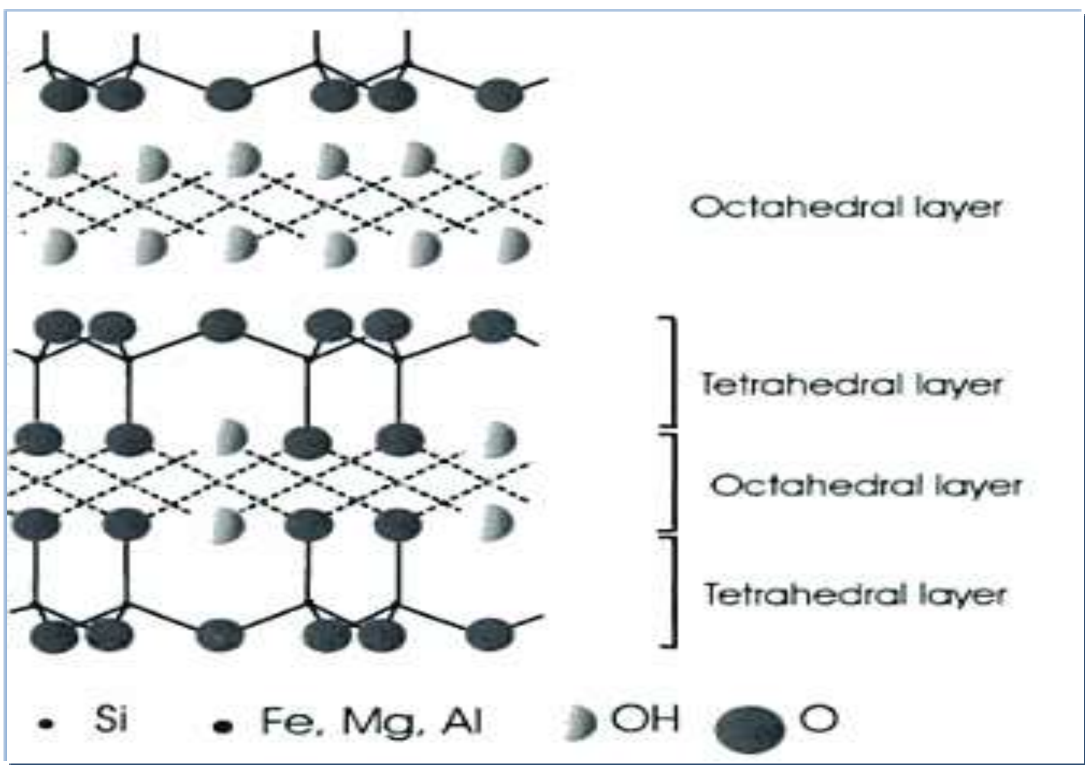

Figure 3.3: Chlorite clay structure

Other silica product, silica flour (see **Figure 3.5**), and additives are used in high temperature wells to improve the quality of cement

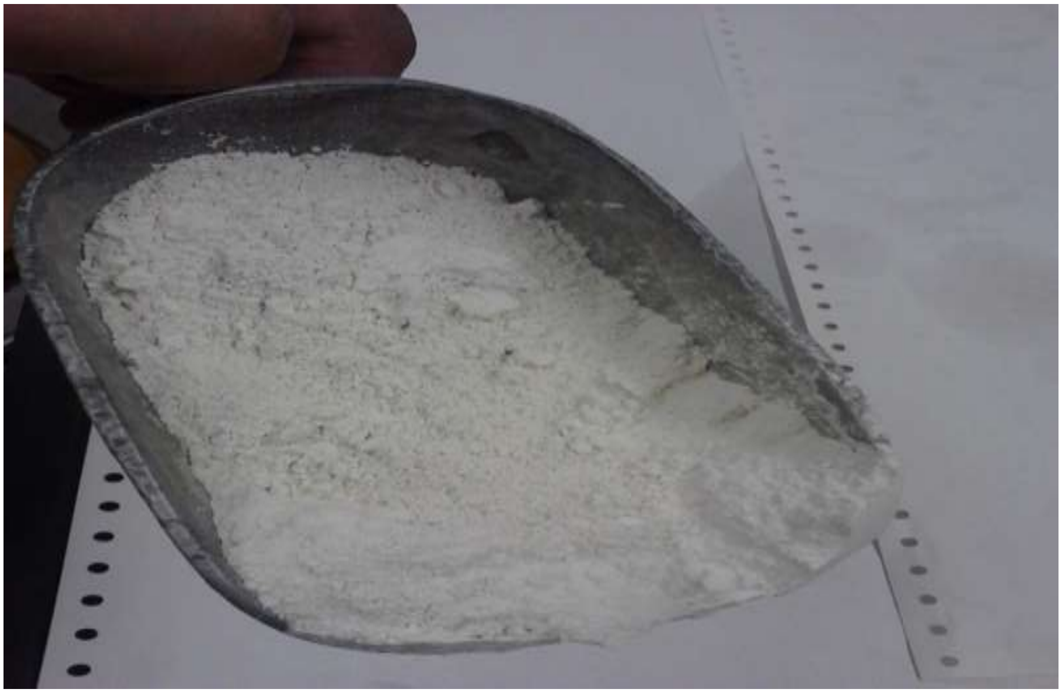

Figure 3.4: Nano clay powder

Figure 3.5: Silica flour powder

3.4 Cement Slurry Preparation

The cement slurry preparation is very important because of the influence of the shear history of the mixture on the properties of cement (Orban *et al*., 1986). The cement slurries is prepared using a variable speed high-shear blender type mixer with bottom drive blades as per the API Specifications (see **Figure 3.7**).

There are two methods of mixing, first is dry mixing in which all additives are dry blended in cement and other is wet mixing, in which additives are mixed in water rather blended in cement. Both methods of mixing are used for different well conditions and location.

In all experiments, wet mixing method has been implemented in which first of all, cement, additives and water weighed depending on the cement design. The cement and silica products are dry blended prior to mixing in water (see **Figure 3.6**). The liquid and dry additives are mixed in tap water at low speed of 4000RPM and cement and silica products dry blended mixture is put in water additive mixture within 15 seconds.

Figure 3.6: Blending of cement with silica products prior mixing

Figure 3.7: High speed blender

The whole slurry is then mixed at high speed of 12000 RPM for 35 seconds in high speed mixer. Later, the cement slurry is conditioned in atmospheric consistometer at 194^{o}F temperature for 20 minutes as shown in **Figure 3.8**. Later, this conditioned slurry can be used for desired tests.

Figure 3.8: Atmospheric consistometer

3.5 Thickening Time Test

The thickening time explains the period within which cement slurry remains pumpable under well simulated conditions (Dwight, 1990). The laboratory test conditions should represent the time, temperature, and pressure to which cement slurry will be exposed during pumping operations. Other factors that can affect the slurry's pumpability during a job cannot be simulated exactly during a laboratory thickening time test (fluid contamination, fluid loss to formation, unforeseen temperature variations, unplanned shutdowns in pumping, etc.).The most commonly used apparatus incorporates a rotating cylindrical slurry container equipped with a stationary paddle assembly, all enclosed in a pressure vessel capable of withstanding well-simulation pressures and temperatures (**Figure 3.9**, API Spec 10A). The slurry container is rotated at a speed of 150RPM. To determine the thickening time, the consistency of cement slurry is measured. The consistency, expressed in Bearden units of consistency (Bc), is determined by the force imposed by the slurry against the paddle and measured as a torque. A potentiometer, or its equivalent, is used to determine the torque.

First the cement slurry is prepared according to API Specifications. The prepared cement slurry is poured in HPHT consistometer cup and placed in HPHT consistometer. After placing, the test conditions are applied. During the thickening time test, increase the temperature and pressure of the cement slurry in the slurry container in accordance with the appropriate well-simulation test schedule. Then the test is conducted up to the time at which the slurry reaches a consistency deemed sufficient to make it unpumpable (for example 70 Bc or 100 Bc). The slurry consistency at which the thickening-time test was terminated should be documented and reported.

After that, the test is terminated and the consistometer is cooled before releasing the pressure. After releasing the pressure, the potentiometer and slurry container are removed and made ready for the next test.

Figure 3.9: HPHT consistometer

3.6 Density of OWC Slurries

The density explains the hydrostatic head of cement slurry in a well. The preferred apparatus for measuring the density of cement slurry is the pressurized fluid density balance (**Figure 3.10**). By pressurizing the sample cup, any entrained air is decreased to a negligible volume, thus providing a slurry density measurement more representative of the true slurry density.

First the cement slurry is prepared according to API Specifications. The slurry is conditioned at atmospheric pressure and 194^{o}F temperature. After the conditioning of slurry, it is poured pressurized mud balance to get the density.

Figure 3.10: Pressurized mud balance

3.7 Free Water Contents

The free fluid test for testing cement slurries used to cement a well helps determine a slurry's capacity to prevent fluid separation in static conditions, both during placement and after it has been placed into the wellbore. Excessive free fluid in slurry can cause problems with water pockets, channeling, sedimentation, zonal isolation, etc.

For the measurement of free water contents, the cement slurry is prepared and conditioned according to API specifications. After the conditioning of cement slurry, the cement is poured in graduated cylinder up to a mark and covered it with aluminum foil to prevent evaporation (see Figure **3.11**). Later, it is subjected to 2 hours test duration. At the end of test duration, a syringe is used to extract the free water separated from the cement slurry and the amount of water is measured in milliliters (ml).

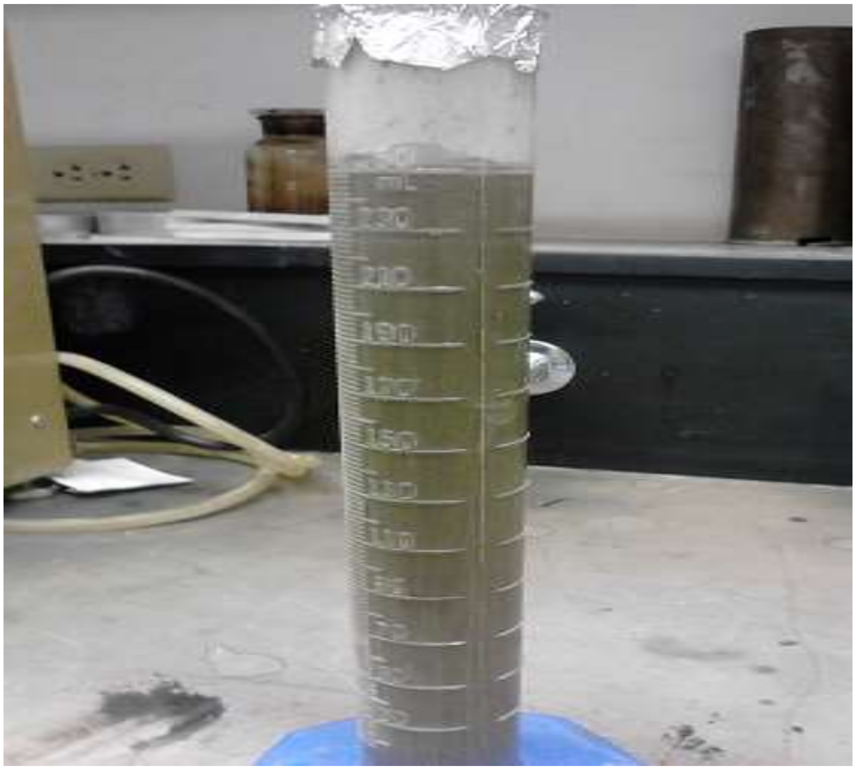

Figure 3.11: Graduated cylinder

3.8 Rheological Properties

The rheology determines the performance of cement and helps in determining the pumpability of cement. In rheology test, apparent flow properties (plastic viscosity, yield point, frictional properties, gel strength, etc.) of a cement slurry are determined, using a rotational viscometer such as HPHT Viscometer by Chandler at high temperature conditions (see **Figure 3.12**).

First of cement slurry is prepared and conditioned according to API specifications. The conditioned slurry is poured in pre-heated cylinder of viscometer at 194^{o}F test temperature. The viscometer is run at different shear rates and at the end of test, in-built software is used to compute the results of plastic viscosity and yield point.

Figure 3.12: HPHT viscometer

The gel strength of a fluid may be measured immediately after determining the rheological properties of the sample or on a separate, freshly-prepared fluid.

First, reconditioning the fluid in the viscometer is done for 1 min at 300 RPM to disperse the gels and to get better measurement of the gel strength. For tests on separate fluids, the cement slurry is prepared, conditioned and loaded in the viscometer. The fluid is then conditioned for 1 min at 300 RPM. Rotor is stopped and slurry is kept static for 10 seconds in viscometer. At the end of 10 seconds, the rotation is resumed at 3 RPM, the maximum deflection obtained is called initial gel or 10 sec gel strength. After this, cement slurry is kept static for 10 minutes, then after resuming, the maximum dial deflection is reported as the 10-min gel strength.

3.9 Compressive Strength of Cement

The compressive strength properties determine the integrity of cement and its ability to bear long term imposed stresses (Adam, 1986). The maximum pressure used for curing is normally 3,000 psi (API), unless otherwise specified. There are two methods to measure the compressive strength, first by crushing and other is by non-destructive method. Compressive strength tests are conducted according to the API Specifications (API Specification-10A, 2012).

3.9.1 Compressive Strength by Crushing Method

The crush strength test indicates the strength of a cement slurry after it has been pumped into the well and allowed to set static. The slurry is subjected to temperature (and normally, pressure) for various lengths of time. The strength test may be performed at bottomhole conditions or the conditions at a specific point of interest (at the top of a long cement column, at the top of a liner, across a producing zone, etc.).

In this test, first of all, the cement slurry is prepared and filled in the chambers of the prepared moulds (**Figure 3.13**), covered with the top plate, and immediately placed in a curing vessel at the desired test initiation temperature (normally 27 °C). Heat and pressure in accordance with the test schedule are applied. In this particular case, test moulds are subjected to the test conditions of 290°F temperature and 3000 psi pressure for 24 hours in HPHT curing vessel (see **Figure 3.14**) . At the end of test duration, the moulds with set cement (see **Figure 3.15**), are removed and cubes are detached from moulds (see **Figure 3.16**). Later, the cubes are crushed in compressive strength tester to get compressive strength results (see **Figure 3.17**).

Figure 3.13: cement moulds

Figure 3.14: HPHT curing machine

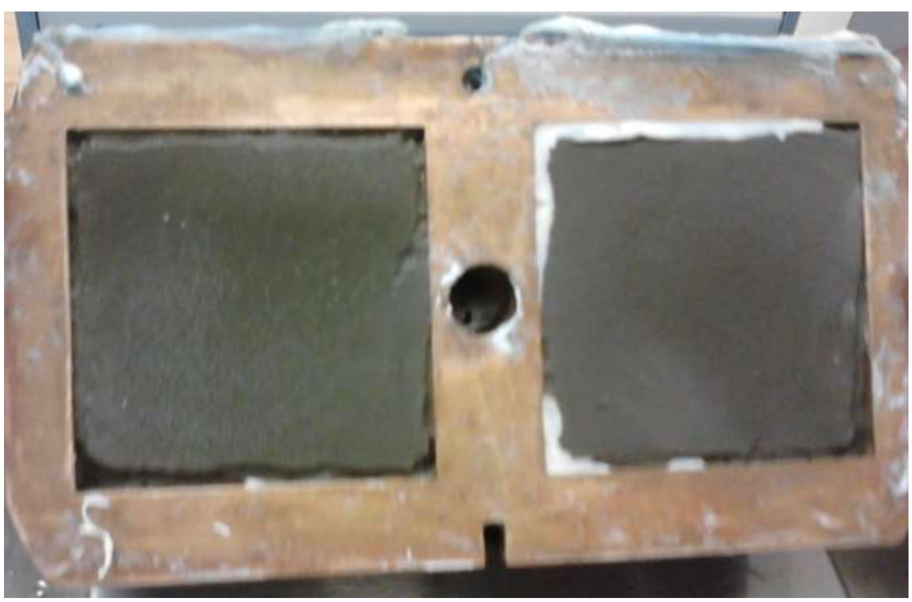

Figure 3.15: Cured cement moulds

Figure 3.16: Cured cubes of cement

Figure 3.17: Crushing of cement cubes using compressive strength tester

Figure 3.18: Samples after crushing

3.9.2 Compressive Strength by Sonic Method

The sonic strength (UCA analyzer) test is a non-destructive test performed on a slurry to estimate its strength. Correlations have been developed to approximate the compressive strength of a cementing composition based on the time required for the ultrasonic signal to pass through the cement as it sets. Sonic strength and crush strength indications can vary considerably, depending on the temperature of the test, slurry composition, etc.

The sonic compressive strength of cement slurry is measured by placing slurry in autoclave unit of ultrasonic cement analyzer (UCA) (**Figure 3.19**) with temperature and pressure adjusted to simulate downhole conditions. An acoustic signal is then transmitted through the cement sample. As the strength of the cement increased over time, the faster the acoustic signal travels through the sample.

First, the cement slurry is prepared and conditioned in atmospheric consistometer for 20 minutes at 150RPM. At the end of conditioning, the cement slurry is poured in the cell of ultrasonic cement analyzer (UCA) (see **Figure 3.20**). The cell is inserted in UCA and applied the test conditions as per the schedule set. Each test is conducted for 48 hours. At the end of test duration, the system is cooled and cement sample is removed from the cell as given in **Figure 3.21**.

Figure 3.19: Ultrasonic cement analyzer

Figure 3.20: Ultrasonic cement analyzer cell

Figure 3.21: Cured sample from UCA

3.10 Permeability and Porosity Tests

Permeability determines the ability of fluid to flow at different pressure and helps in determining the long term performance of cement. The cement sheath is supposed to seal the zones and prevents fluid migration under HTHP conditions, which is only possible if we have low permeability. Porosity determines the void spaces where fluid is stored and later affects the properties of cement sheath.

The 1″×1″ cylindrical cement plugs are drilled out from the cubes of cement as shown in **Figure 3.22** . The cement plugs are dried for a day. After that, gas permeability and porosity tests are conducted on the Automated Porosimeter/Permeameter (**Figure 3.23**) at 500psi confining pressure.

This Automated Porosimeter/Permeameter (AP-608) is a state of the art system for measuring gas permeability and porosity of rock core samples under realistic reservoir conditions. The AP-608 comes complete with manually loaded hassler type coreholder and inserts for either 1.5″ or 1.0″ of diameters are supplied.

The permeability measurements are made using an unsteady state pulse decay technique. The permeability range of the AP-608 is from 5000md to 0.001md.

Figure 3.22: Cement plugs

Figure 3.23: Automatic porosimeter/ permeameter

3.11 Microstructural Analysis

The microstructure of cement slurry is studied using both SEM and XRD analysis. SEM explains the composition, topography and pore structure and XRD is a well-known technique for studying cement composition and hydration. Using XRD spectra, several compounds in hydrated cement paste such as alite (C_3S), belite (C_2S), ettringite (AFt), calcium hydroxide (CH, portlandite) and calcium silicate hydrate(C-S-H), tobermorite etc. can be detected. For the XRD analysis, the cement samples are crushed to powder form and in SEM analysis, the small pieces of cement samples are used.

CHAPTER 4

RESULTS AND DISCUSSIONS

This chapter describes the results of study on the effect of Nano clay on Portland Saudi cement type 'G' properties in high pressure and temperature applications. The results of each experimental test are discussed here for the proposed Nano clay percentages of the selected well cement system.

4.1 Cement System Validation

The two cement designs were proposed in Chapter 3, where the only difference between the two designs was the addition of Nano clay in various percentages proposed to be (0, 1, 2, 3 & 4) % BWOC.

After conducting the experimental program, the following observations were made;

The cement slurry design of without Nano clay was first implemented with 0.4%BWOC dispersant. With this design, the cement slurry was thick and its viscosity was high that it was out of range on Fann Viscometer that it might cause high pressure losses. For this reason, the dispersant percentage was increased to 0.8%BWOC for its easy mixing and to reduce its viscosity. The rheological properties were in acceptable range using the 0.8%BWOC dispersant. So, dispersant percentage (0.8%BWOC) was kept constant in all other experiments. It was observed that improved cement slurry design without Nano clay (**Table 3.2**) was easy to implement in the lab and the slurry mixture was easy to condition, test, and clean.

Cement slurry design with Nano clay was more challenging than the slurry design without the Nano clay addition as the presence of Nano clay affected the cement physical properties, "The more the Nano clay added, the thicker the slurry would be".

Cement slurry design having Nano clay percentage of (4.0%) wasn't successful as the slurry materials were difficult to mix with same water cement ratio and dispersant percentage because the addition of Nano clay absorbed more water for its mixing. The behavior is caused by small size and high surface area of Nano clay particles those cause the high friction between particles and amalgamates the particles.

To mix the 4% Nano clay cement system, the water cement ratio must be increased for easy mix on the compromise of other properties of cement as compressive strength is affected by WCR. The purpose is to design and evaluate the Nano clay effects without modifying the base design parameters so that comparison can be made without trouble. So, 4% Nano clay cement mix would not be considered for further testing.

4.2 Effect of Nano Clay on Thickening Time

Thickening time test determines the time period in which slurry remains pumpable. If the cement slurry works as a liquid over extended period of time and functions as a solid when it stops flowing, it might be suitable for more of jobs. This test was conducted using HPHT consistometer according to API specifications (2012). The pressure was set at 64MPa and the temperature at 228^{o}F. The time for heating rate was 42 minutes.

The four cement systems having Nano clay percentages of (0 %, 1.0 %, 2.0 % & 3%)BWOC were subjected to thickening time test and time of cement slurries to reach a consistency of 100 Bc were recorded.

Figure 4.1 to **Figure 4.4** explain the thickening time results of (0%, 1%, 2% & 3%) BWOC Nano clay cement systems. It is investigated that all four cement systems have (77, 80, 93 & 99) Bc consistencies at the start of tests which indirectly represent the viscosities at the start of test (see Figure **4.7**). When the test conditions are implemented, the viscosities are reduced and stabilized for some period of time until 100Bc consistency achieved where they are considered unpumpable.

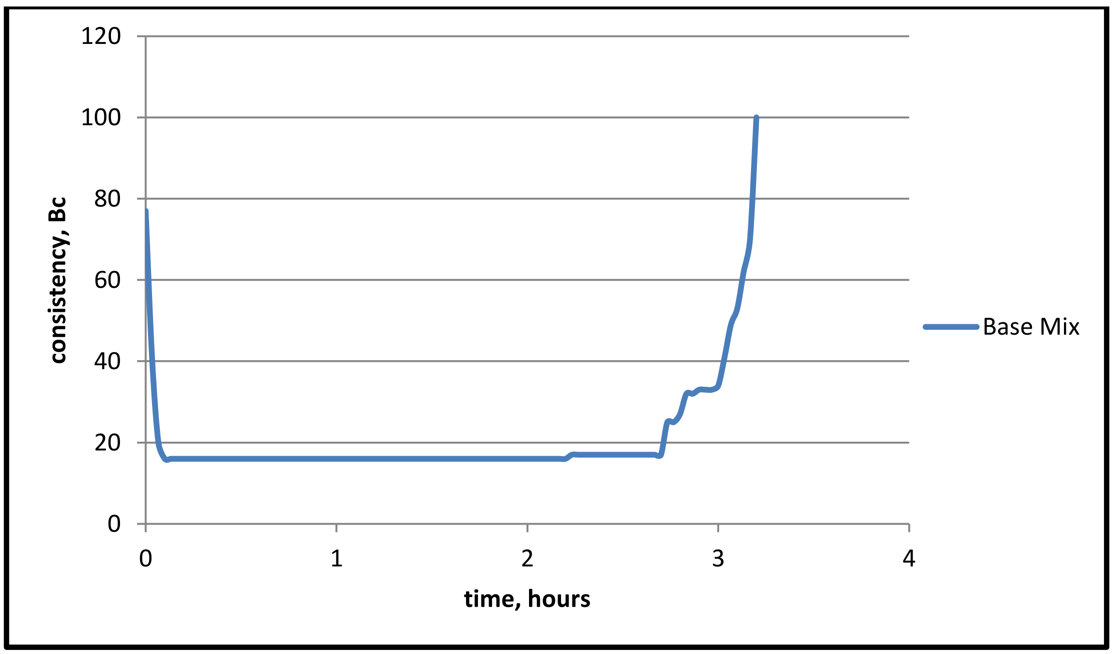

Figure 4.1: Thickening time plot of base mix (0% Nano clay)

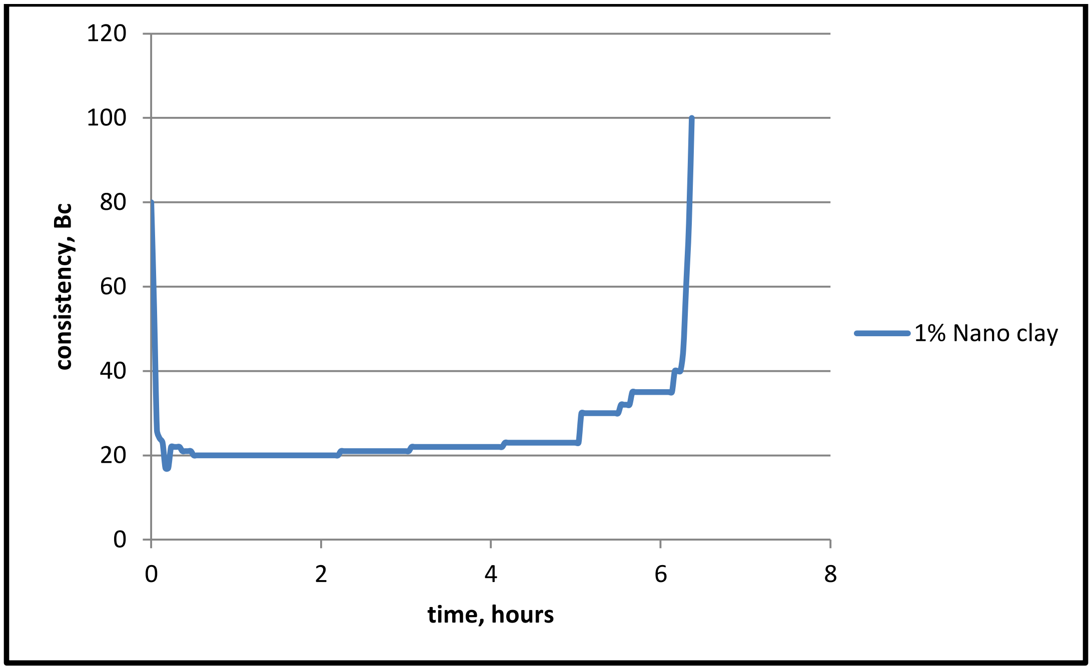

Figure 4.2: Thickening time plot of 1% Nano clay cement slurry

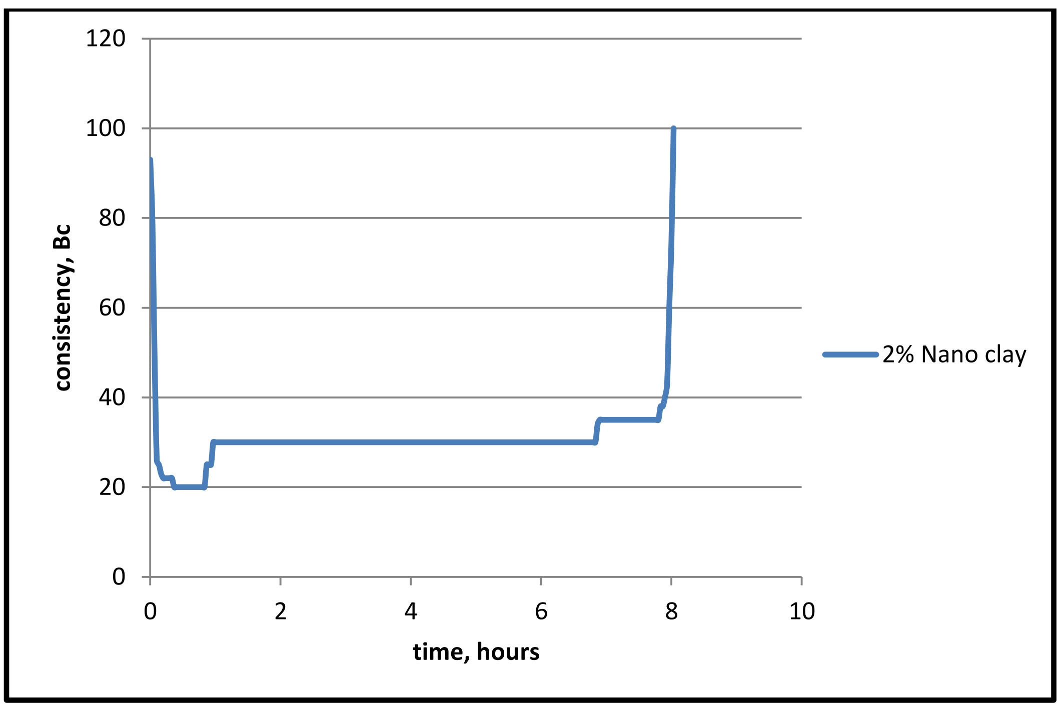

Figure 4.3: Thickening time plot of 2% Nano clay cement slurry

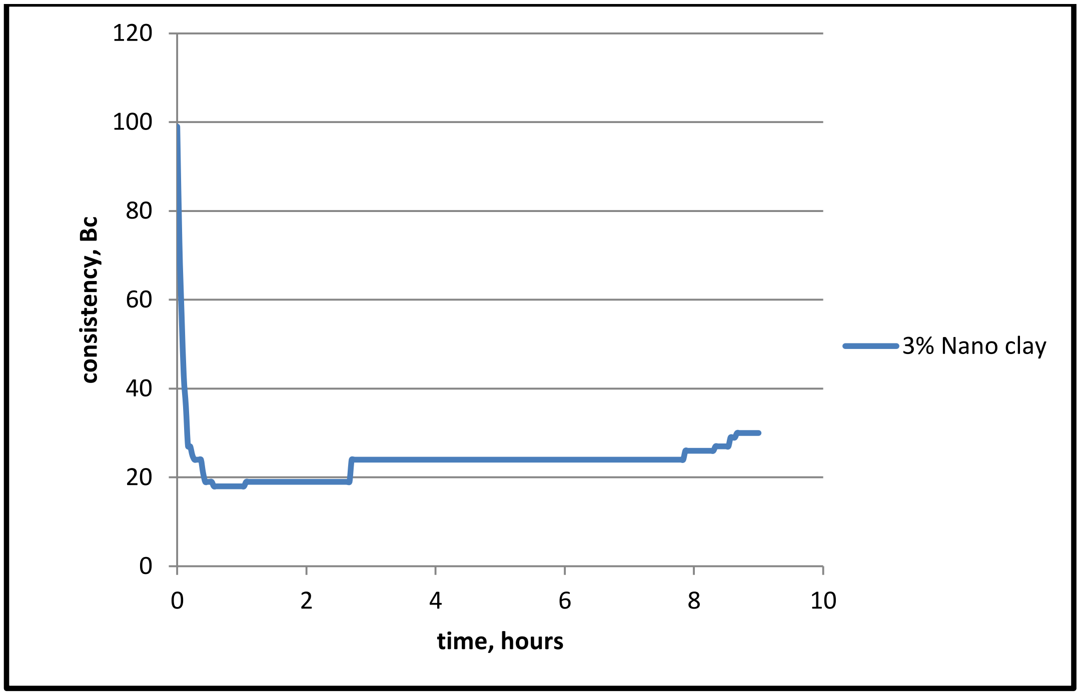

Figure 4.4: Thickening time plot of 3% Nano clay cement slurry

Figure 4.5 explains the thickening time test plot of all cement systems containing (0, 1, 2& 3) % BWOC Nano clay. It is observed that addition of Nano clay resulted increase in thickening time of slurries. The addition of Nano clay slows down the hydration of cement and retards the cement slurries as it can be perceived that 3% Nano clay system does not attain thickening time even after 9 hours.

The addition of 1% Nano clay increases the thickening time from 3 hours, thickening time of base slurry, to six hours. The further addition of Nano clay by 2% BWOC increases the thickening time around 8 hours. So, it can be evaluated that Nano clay acts as retarder that helps in deep well cementing by retarding the thickening time.

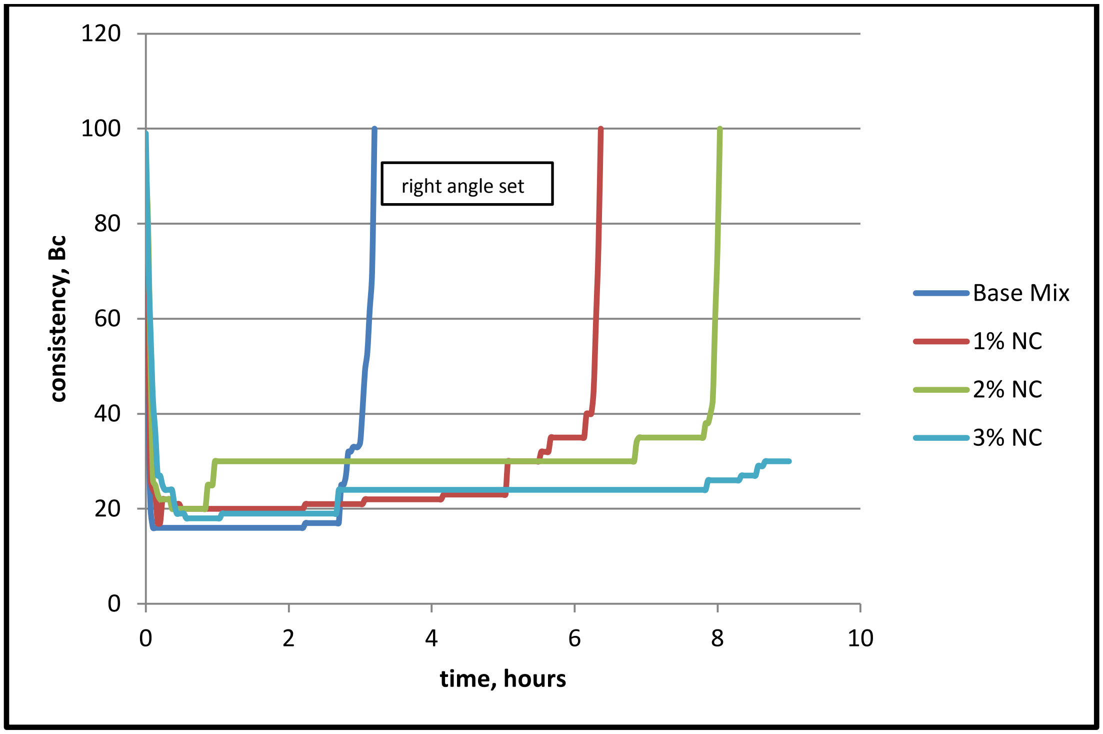

Figure 4.5: Variation of thickening time at different Nano clay concentrations (0, 1, 2& 3) %BWOC

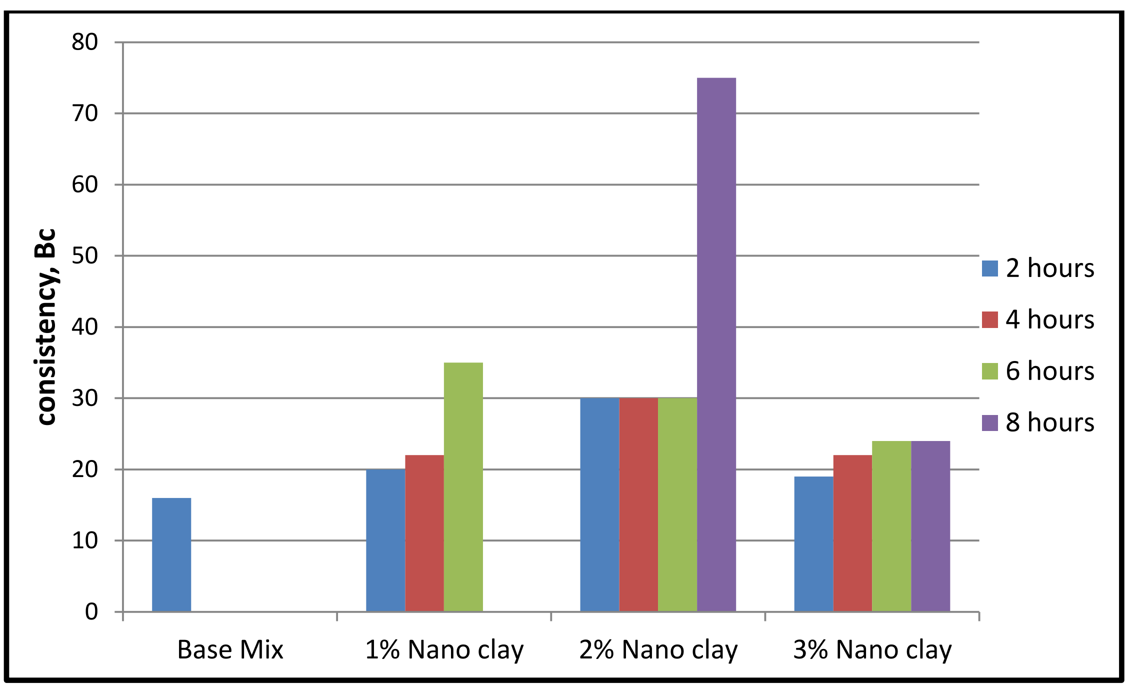

Figure 4.6: Consistencies at different time durations (2, 4, 6& 8) hours

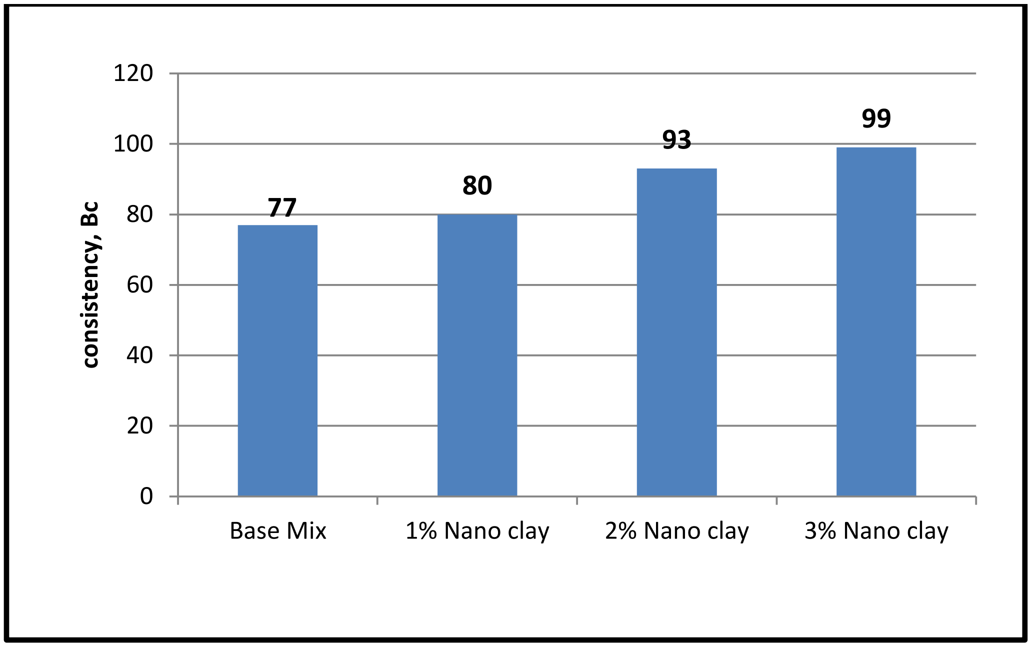

Figure 4.7: Consistencies at the start of test

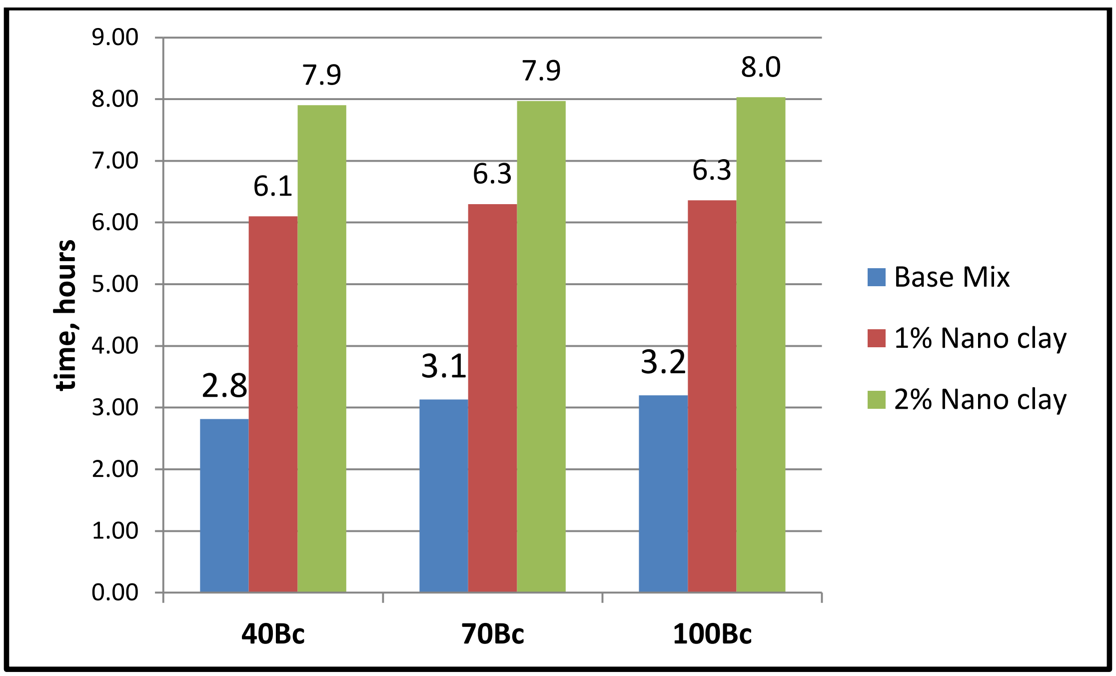

Figure 4.8: Time to reach 40Bc, 70Bc and 100Bc consistencies

From Figure **4.8**, it can be investigated that it takes a long time to achieve 40Bc consistency for all slurries. When all slurries approach 40Bc then time to get 100Bc is very short in all cement mix. This point is called right angle set as it takes minimum time to reach 100Bc consistency. So, it can be concluded that 40Bc is point after which slurries can be considered unpumpable because short time span between 40Bc and 100Bc.

4.3 Effect of Nano Clay on Free Water Separation

Free water is water that might be separated from the cement slurry and accumulated at top of cement while particles settling effect could take place.

To determine the effect of Nano clay on the amount of free water of cement slurry, the four cement systems having Nano clay percentages of (0 %, 1.0 %, 2.0 % &3%) and simple Class G cement have been subjected to free water test where they have been aged for 2 hours under normal room temperature and atmospheric pressure. From **Table** 4.1 results, it is evident that simple Class G cement cannot be injected alone in high pressure and temperature wells as it causes the free water separation at the top of cement which results in particle settling and low hydrostatic pressure of cement column. It is necessary to incorporate the additives in Class G cement to design slurry for HPHT wells. Later, 35% silica flour was mixed in simple class G cement and subjected to free water content test. It was observed only addition of silica flour resulted in no free water contents which showed ability of silica flour to absorb more water.

The cement systems are designed containing different percentages of Nano clay. When these systems are subjected to free water separation tests, they all show no water separation at the top of cement column (see Figure **4.9**).

The reason of no water separation is the small size particles of Nano clay which block the capillaries and prevent water separation. By this way, the hydrostatic pressure of cement column remains constant and it does not reduce to affect the balance of pressures of the well.

Even the Nano silica admixed cement system does not show the free water separated at the top of cement column which is because of small size of Nano silica that caused filling of the capillaries in cement and restricts the flow of water. From the experimental results, it can be concluded that both Nano silica and Nano clay materials are very effective in reducing the free water contents.

Table 4.1: Variation of Free water contents of cement slurries containing (0%, 1%, 2% &3%) Nano clay and 1% Nano silica

Free Water	**G Class**	**G+35%SF**	**Nano clay percentages BWOC**					
			Base Mix	1%NC	2%NC	3%NC	1%NS	G+3%NC
ml/250ml	2.1	0	0	0	0	0	0	0

Figure 4.9: Free water separation test

4.4 Effect of Nano Clay on the Rheological Properties

The rheological properties of an oil well cement (OWC) slurry defines the quality of the final product and assists predicting its end use performance and physical properties during and after processing. Rheological measurements can determine the flow properties of the cement slurry such as plastic viscosity, yield point, frictional properties, gel strength, etc. Rheology studies the flow of fluids and deformation of solids under stress and strain.

Table 4.2 presents the rheological results of different Nano clay percentages (0%, 1%, 2% &3%) BWOC with simple class G and Nano silica rheology. It is evident from the results that simple G class cement slurry has low rheological properties that it cannot improve the mud displacement in these particular well conditions. The cement system has been designed for a particular well depending on its condition (see **Table** 3.2). Different kinds of additives are incorporated in Class G cement to improve its rheological properties. Later, Nano clay is incorporated in different percentages to base slurry and subjected to rheology test.

It is observed that addition of Nano clay to the base slurry caused improvement in rheological properties (PV and YP). **Figure 4.10** and **Figure 4.11** show the trends of rheological properties changes. It should be noted that upturn in Nano clay percentage results in thicken of cement slurry. It is obvious that the addition of Nano clay to base cement system results in rise of plastic viscosity of cement. As the plastic viscosity is a function of solid particles so the addition of Nano clay to cement increases the solid particles which in turn enhance the viscosity. The change in yield point is not much up to the addition of 2% Nano clay (see **Figure 4.11**). As the Nano clay percentage is increased to 3%BWOC, the yield point is increased to 16.4 $lb_f/100ft^2$. So, the optimum mixture should be designed with caution as it affects the other properties of cement.

Later, the Nano silica is subjected to rheology test and it is observed that Nano silica improves the rheology of slurry. From the comparison of rheological properties between Nano clay and Nano silica, it can be investigated that addition of 1% Nano silica enhances the viscosity of cement slurry more than the Nano clay addition. The reason of this improvement in viscosity is the very small particle size and high surface area of Nano silica which create more friction in pumping. From the experimental results, it can be evaluated that Nano silica is more viscosifier than Nano clay. The Nano silica effect on yield point is very prominent as it resulted in high yield point at its low percentage.

Table 4.2: Rheology of Nano clay admixed cement slurries at HPHT

Properties	Class G	Base Mix	1% NC	2% NC	3% NC	1% NS
Plastic Viscosity(cP)	32.24	131.14	205.52	229	244.64	224.59
Yield Point $lb_f/100ft^2$	16.4	9.65	9.45	12.6	16.44	27

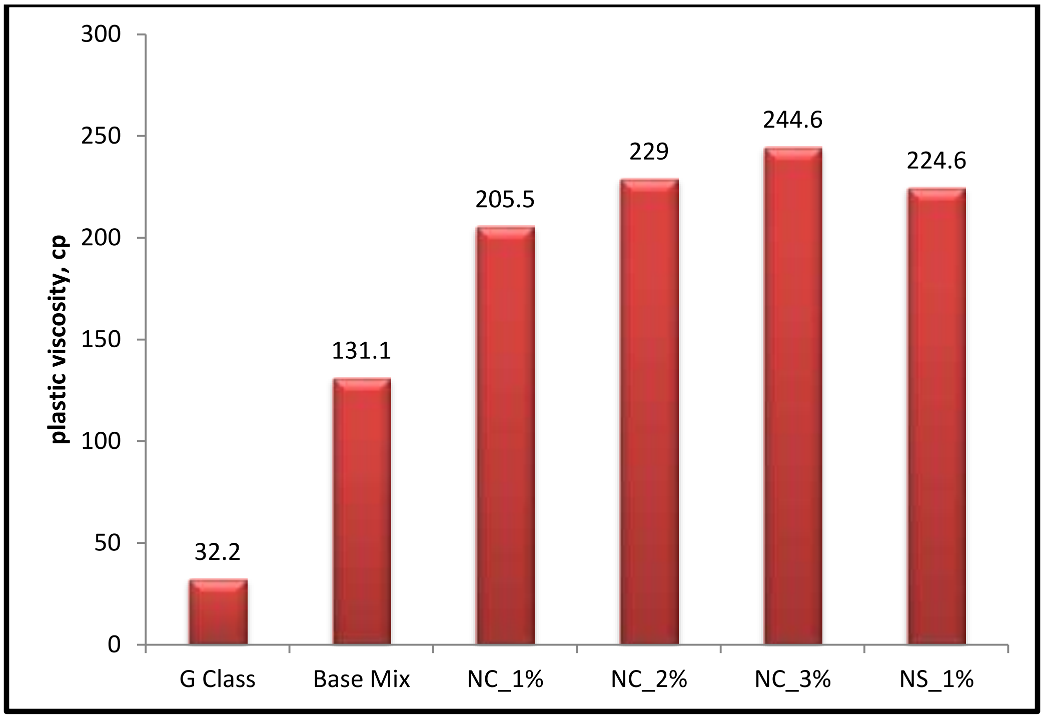

Figure 4.10: Plastic viscosity variation for different concentrations of Nano clay

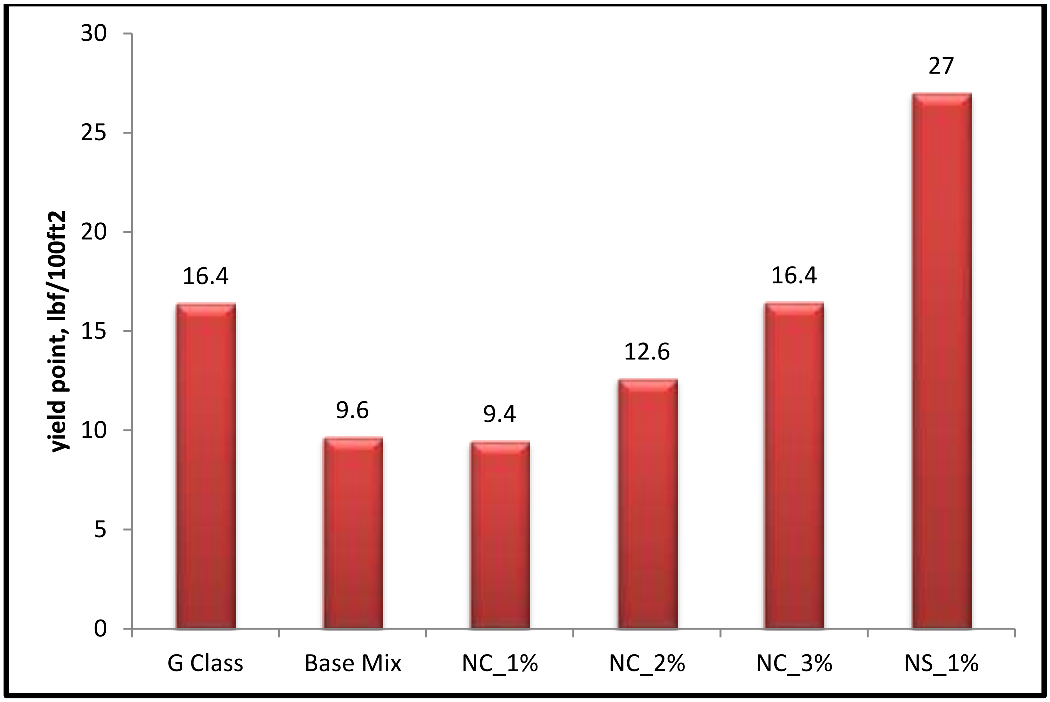

Figure 4.11: Yield point variation for different concentrations of Nano clay

Later, all cement systems are subjected to gel strength tests which is measure of the attractive forces in particles that cause the development of gelation when flow is stopped. It also explains the force required to initiate the flow after stopping circulation.

Gel strength test is conducted on Fann Viscometer and results are provided in **Table 4.3**. It is evident from the results that the addition of Nano clay in base cement results in change in gel strength. The Nano clay addition does not put prominent effects on the initial gel strength, 10- sec, as the results are almost same in (0, 1& 2) % Nano clay cement systems. But the further addition by 3% Nano clay improves the 10-sec gel strength to $13lb_f/100ft^2$.

When the Nano clay cement systems are subjected to 10-min gel strength, they affect the gelling behavior of cement slurries. It can be evaluated from the results that up to 2%

BWOC Nano clay cement systems the 10-min gel strength results are almost similar. But the further addition of Nano clay by 3%BWOC increases the gel strength to 35$lb_f/100ft^2$ from 29 $lb_f/100ft^2$ (see **Figure 4.12**).

When the Nano silica behavior is analyzed on the gel strength, it is obvious that small percent of Nano silica is more effective than high percent of Nano clay. Nano silica develops gel strength fastly and can help in reducing particles settling. So, it can be observed that Nano clay and Nano silica addition helps in formation of early gel strength.

Table 4.3: Gel strengths results of G class, (0,1,2,3)% Nano clay and Nano silica admixed slurries

Gel Strength $lb_f/100ft^2$	**Class G**	**Base Mix**	**1% NC**	**2% NC**	**3% NC**	**1% NS**
10-sec	7	9	9.5	10	13	15
10-min	20	27	27	29	35	38

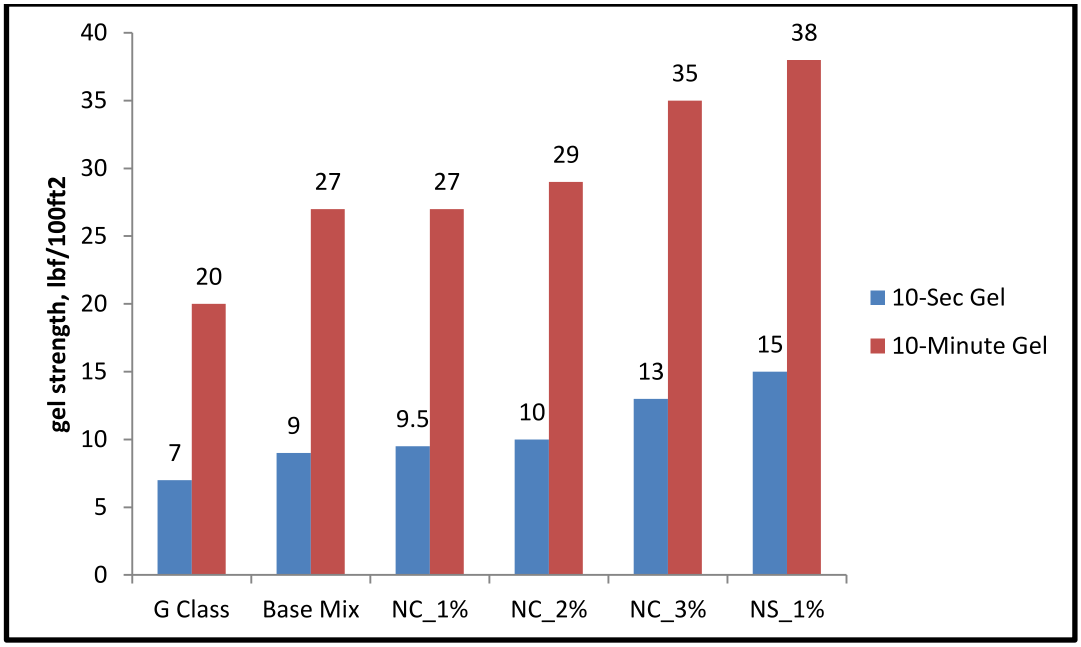

Figure 4.12: Effect of Nano clay and Nano silica on gel strength

4.5 Effect of Nano Clay on Density

The density of neat cement slurry, i.e., mixture of water and cement, varies from 1773 kg/m^3 (110 lb/ft^3) to 1965 kg/m^3 (123 lb/ft^3) depending on the API Class of the cement and the water/cement ratio (w/c). Higher density cement slurry may be required to control well fluids subjected to high bottomhole formation pressures. It is required to increase the density of OWC slurries to diminish the diffusion of heavy drilling muds. The density of the cement slurry is usually measured by pressurized mud balance in the laboratory. The cement slurry is designed with reference of 16.6lb/gal cement slurry of the selected well. The Nano clay admixed cement slurries are subjected to density measurements. The densities of four cement slurry systems having (0%, 1%, 2% & 3%) Nano clay percentages and Class G cement slurry are measured in the laboratory (see **Table 4.4**).

Table 4.4: Densities of slurries having (0%, 1%, 2% & 3%) Nano clay

Slurry Type	**Density**
	lb/gal
Class G	15.8
Base Mix	16.59
1% NC	16.5
2% NC	16.4
3% NC	16.2
1%NS	16

The density of cement slurry can be controlled by either water cement ratio or weighing agents. Depending on the selected well conditions, the Class G cement does not give required density to bear the pressure of deep wells. So certain additives are incorporated in class G cement to design required slurry. The cement system without Nano clay gives the density of 16.59 lb/gal value. When Nano clay is incorporated in base cement design, it decreases the density of cement slurry. But the addition of Nano clay does not reduce the density value appreciably as the density of cement slurry having 3% Nano clay is just reduced by 1.25% from the base cement of 0% Nano clay. So it proves that the Nano clay material does not put noticeable effect on the density of cement as shown in the Figure **4.13**. But as Nano silica is mixed in cement by 1%BWOC, the cement density is reduced to 16lb/gal. This change in density explains that Nano silica being lightest material helps in reducing the density of cement and can be used in designing the light weight cement slurries.

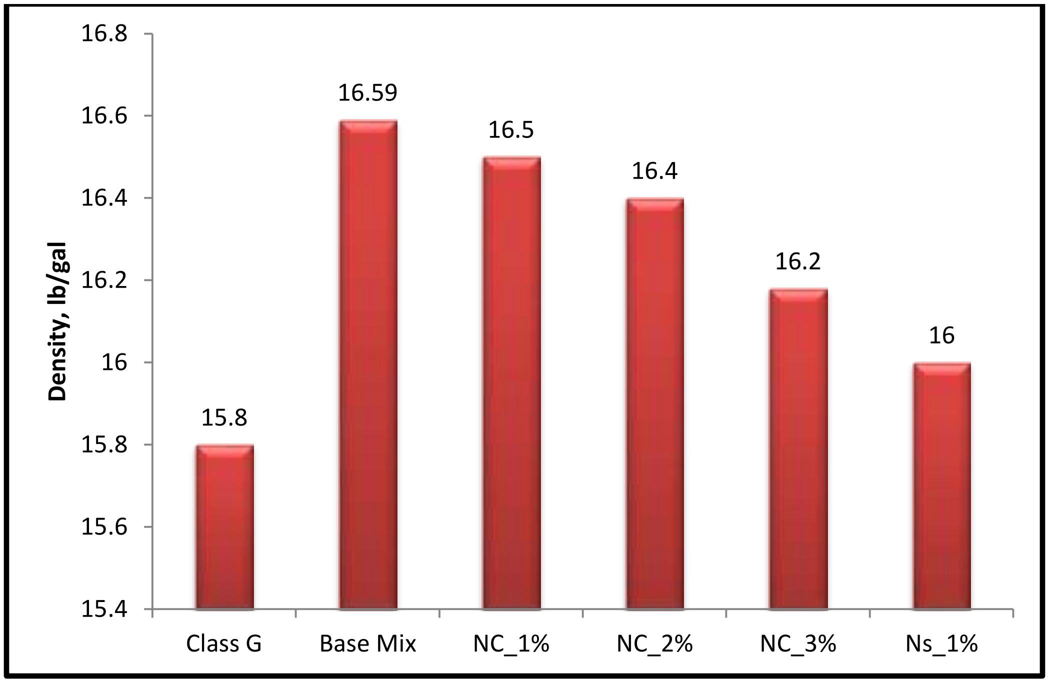

Figure 4.13: Density variation on addition of different Nano clay percentages and Nano silica

It should also be noted that density values reported here might be subjected to human measurement skills or density balance calibration accuracy.

4.6 Effect of Nano Clay on Compressive Strength

The compressive strength properties measure the integrity and stability of cement to sustain long term imposed stresses. Cement slurry is supposed to develop the compressive strength early and make strong bond with walls of well after the placement. So that the drilling operations can be resumed in short time. The pumping of cement efficiently, placing it safely on time, assuring cement integrity after placement (prior to resuming drilling operation) are all issues to be considered. Therefore, compressive strength tests are conducted to evaluate the development of cement strength with time utilizing the ultrasonic cement analyzer (UCA) and also to determine cement bonding stability after set utilizing the conventional compressive strength test (Crushing).

4.6.1 Non-Destructive Compressive Strength by Ultrasonic Cement Analyzer

The five cement systems having Nano clay percentages of (0 %, 1.0 %, 2.0 %, 3%& 4%) and simple Class G cement have been subjected to the ultra sonic cement analyzer (UCA) test under high temperature (290 °F) and pressure (4666 Psi) for 48 hours.

By Ultrasonic cement analyzer method, three different properties of cement slurries can be evaluated such compressive strength (green), transit time (blue) and acoustic impedance (aqua) on the chart.

When a cement slurry is subjected to high temperature and pressure conditions, it starts developing its compressive strength with time. As cement develops compressive strength, it transit time reduces and its acoustic impedance starts increasing. Transit time and acoustic impedance properties help in cement bond logging and in determining cement bond with formation and casing.

From the test results, it is evident that when simple Class G cement is subjected to high temperature and pressure conditions, the compressive strength development is very high at the start which shows the fast hydration and setting of Class G cement. This development of compressive strength does not stay longer as after 12 hours the rise in compressive strength is quite low and it gets stable till the end of 24 hours (see **Figure 4.14**). So it can be concluded that when Class G cement is subjected to high temperatures in excess of 230°F, the hydrated Portland cement undergoes significant phase changes which results in substantial decrease in compressive strength of the cement slurry. The cementing of deep wells with high temperature and pressure conditions requires the addition of special materials in the cement slurry to counteract the degradation of compressive strength. To combat strength retrogression in cement sheath and to reduce permeability at high temperature, silica flour in the range of 30%-40% is added to Portland cement (Iverson et al. 2010).

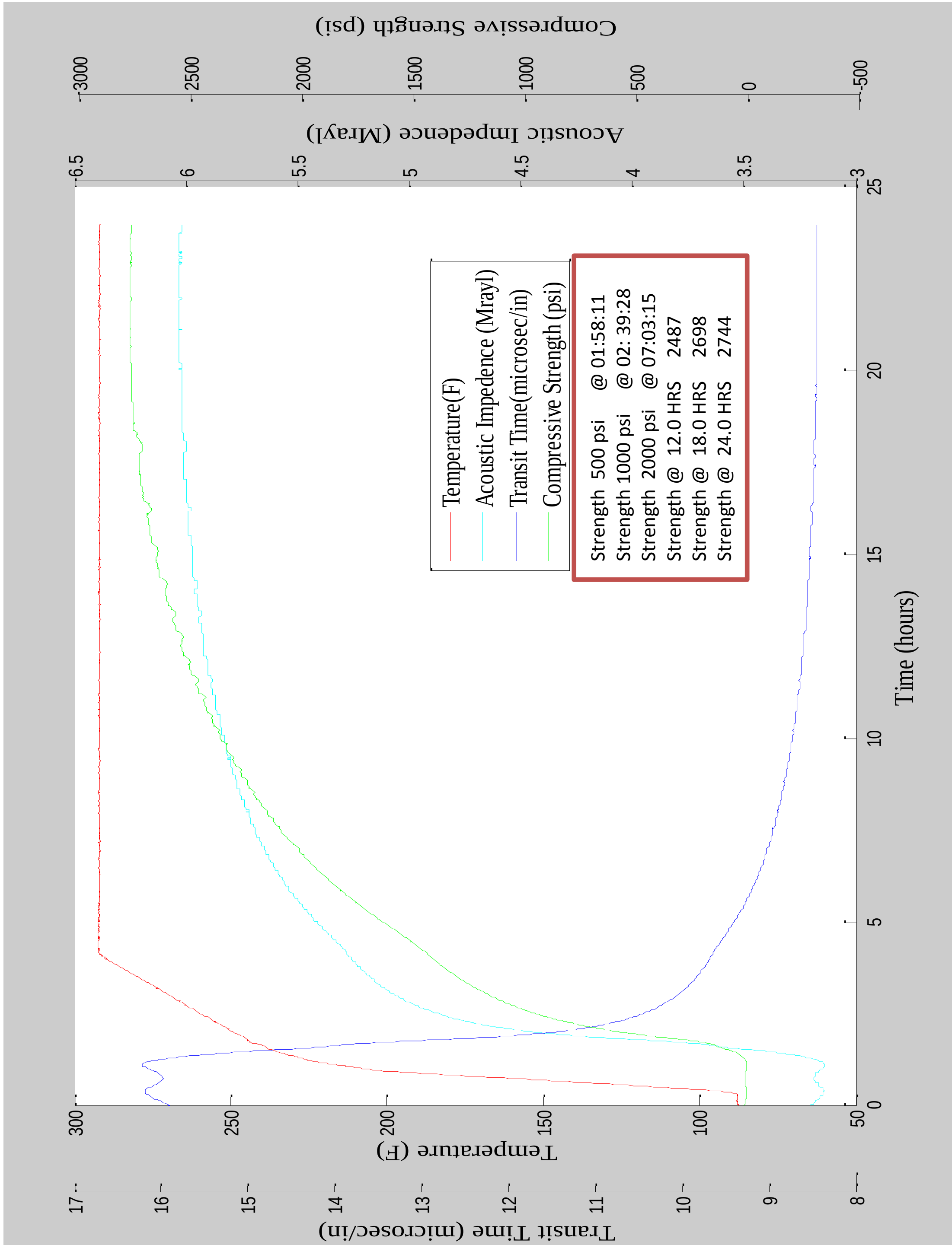

Figure 4.14: Compressive strength development of simple class G cement at HPHT

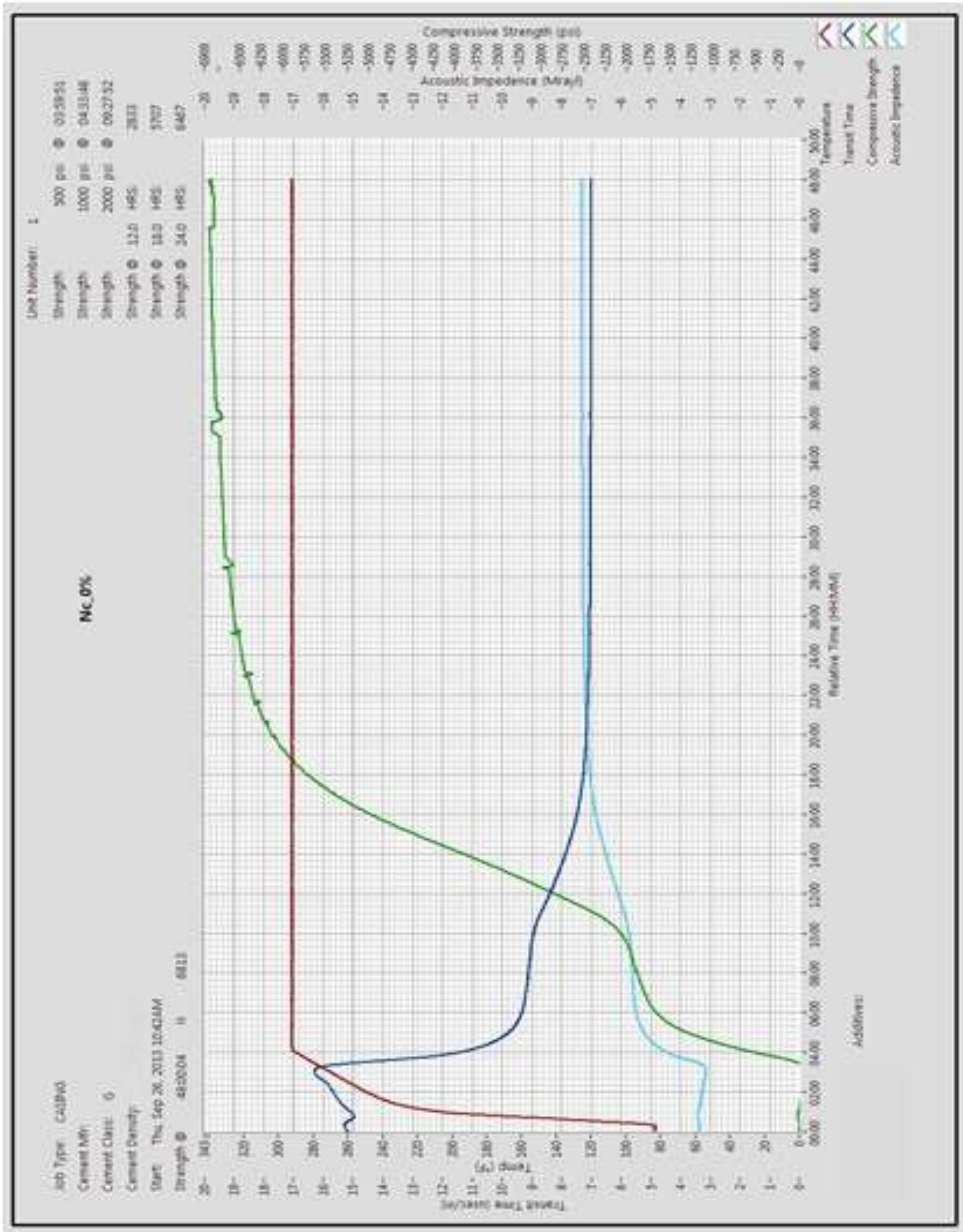

Figure 4.15: Compressive strength development of Base Mix (0% Nano clay) cement slurry at HPHT

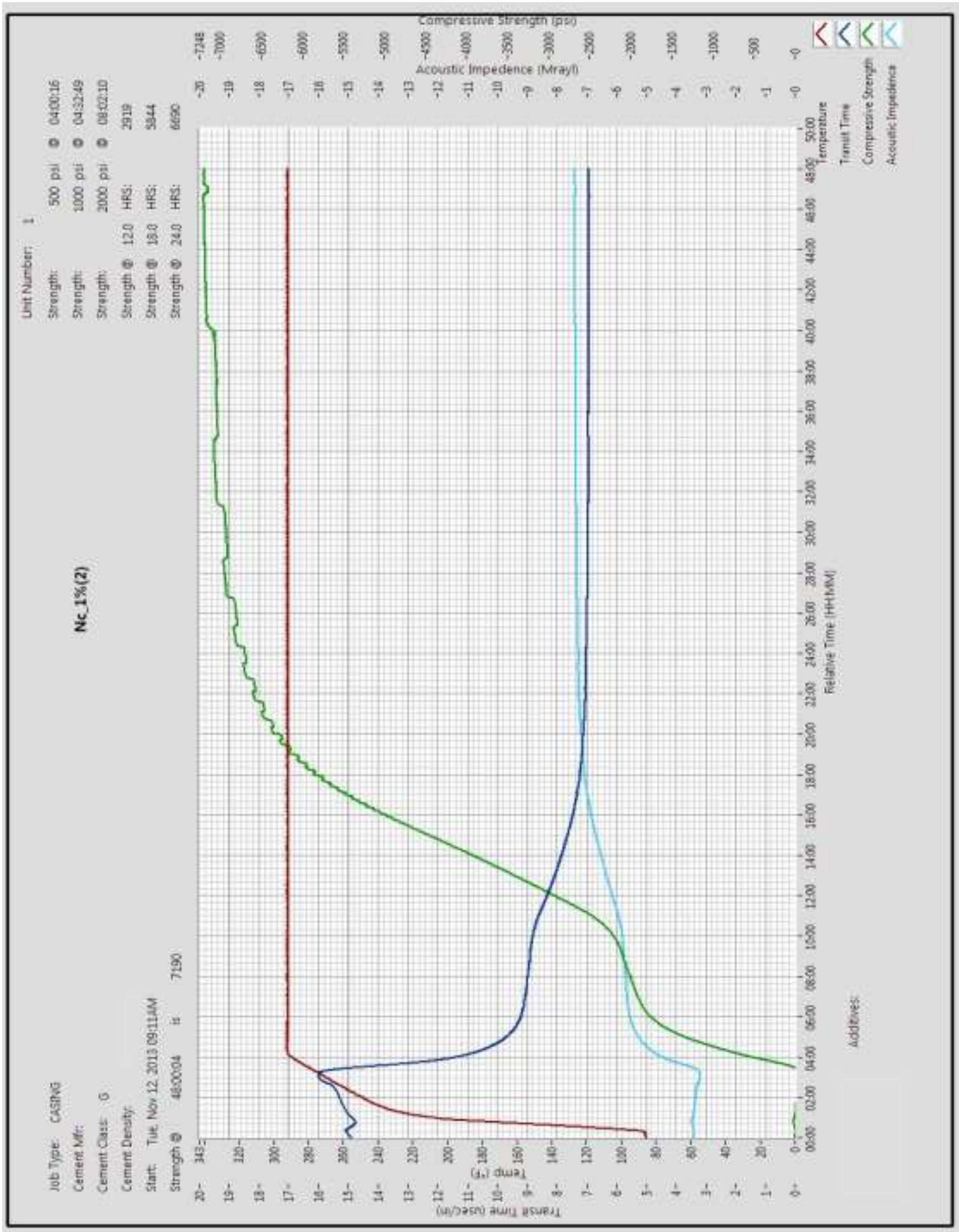

Figure 4.16: Compressive strength development of 1% Nano clay cement slurry at HPHT

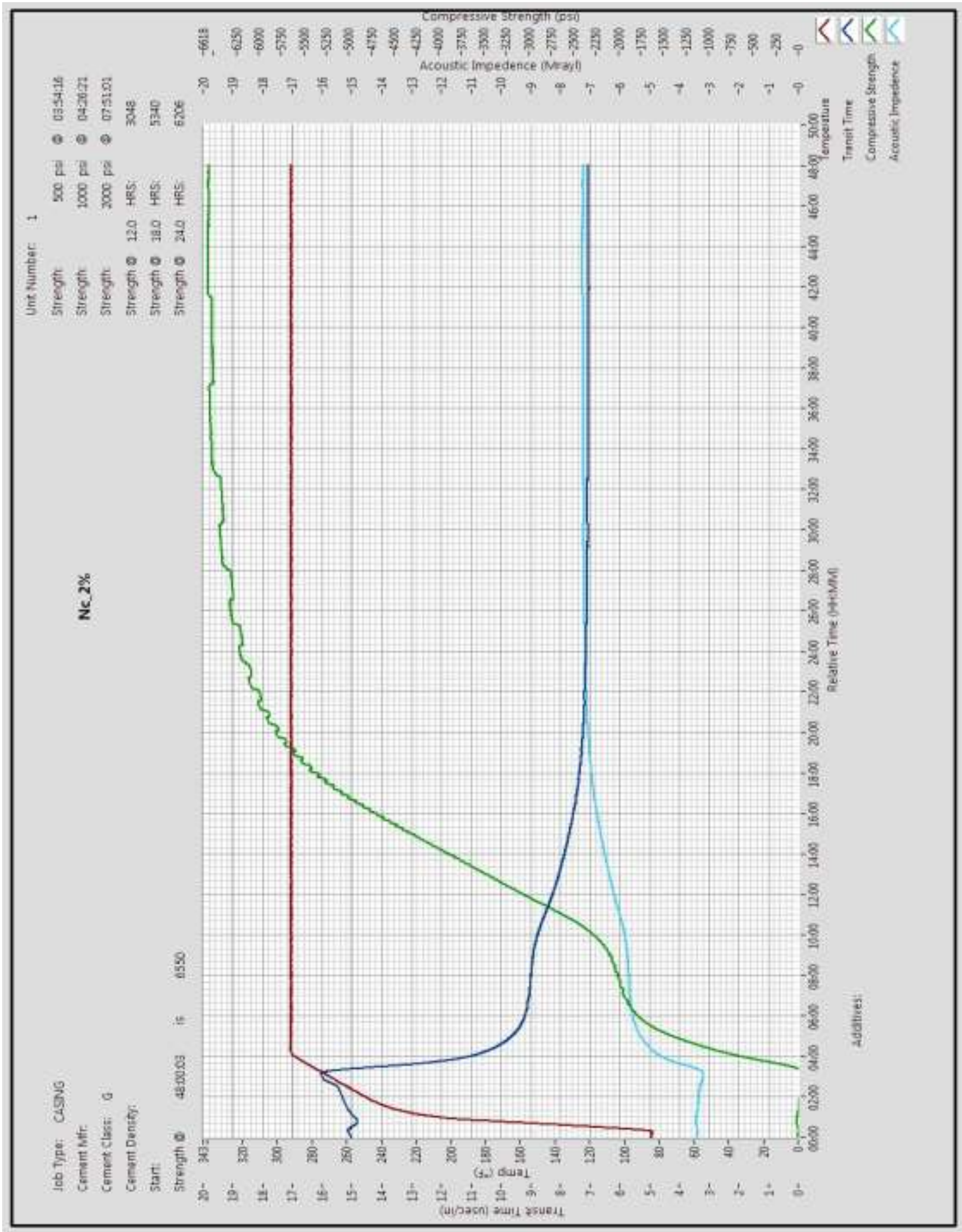

Figure 4.17: Compressive strength development of 2% Nano clay cement slurry at HPHT

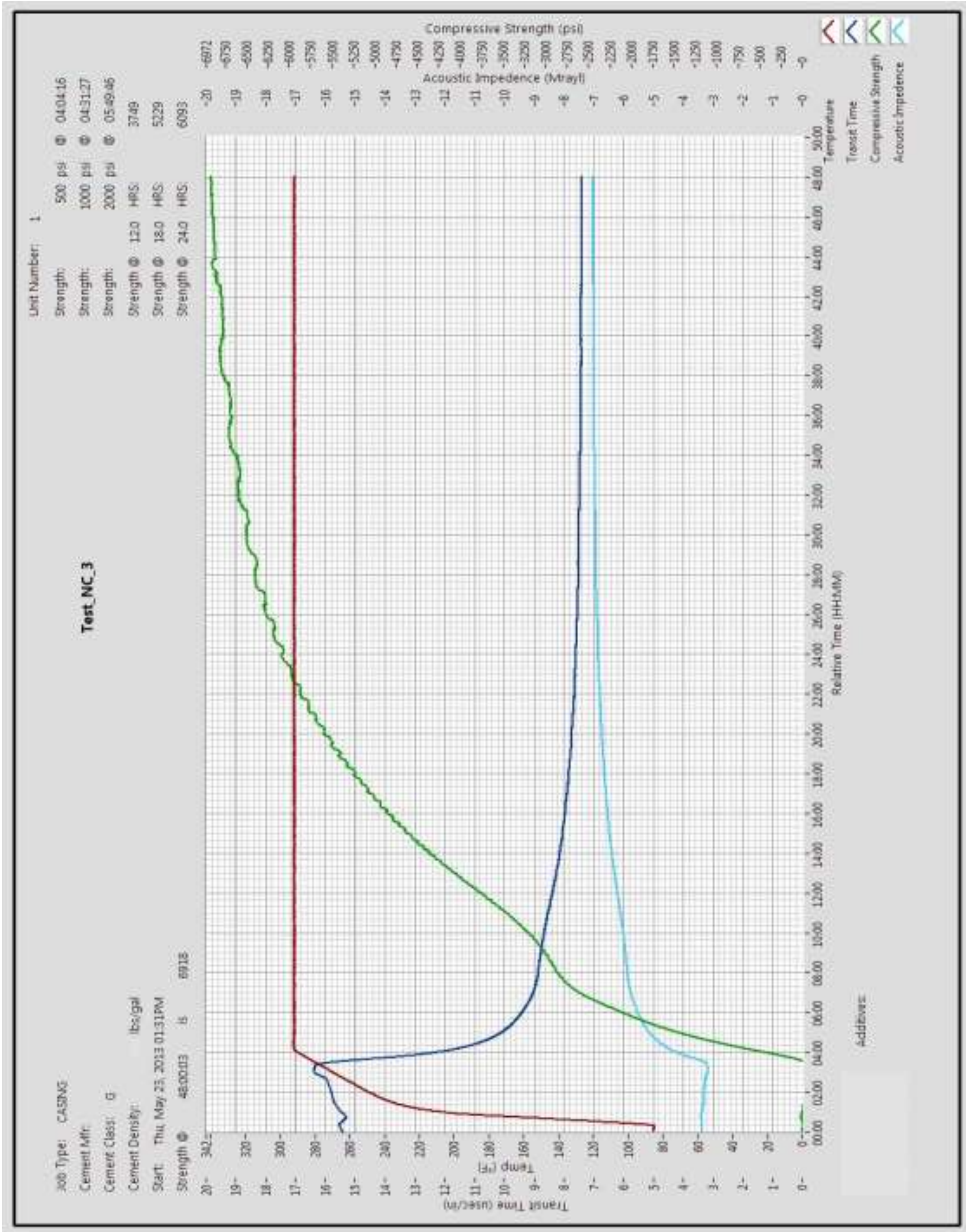

Figure 4.18: Compressive strength development of 3% Nano clay cement slurry at HPHT

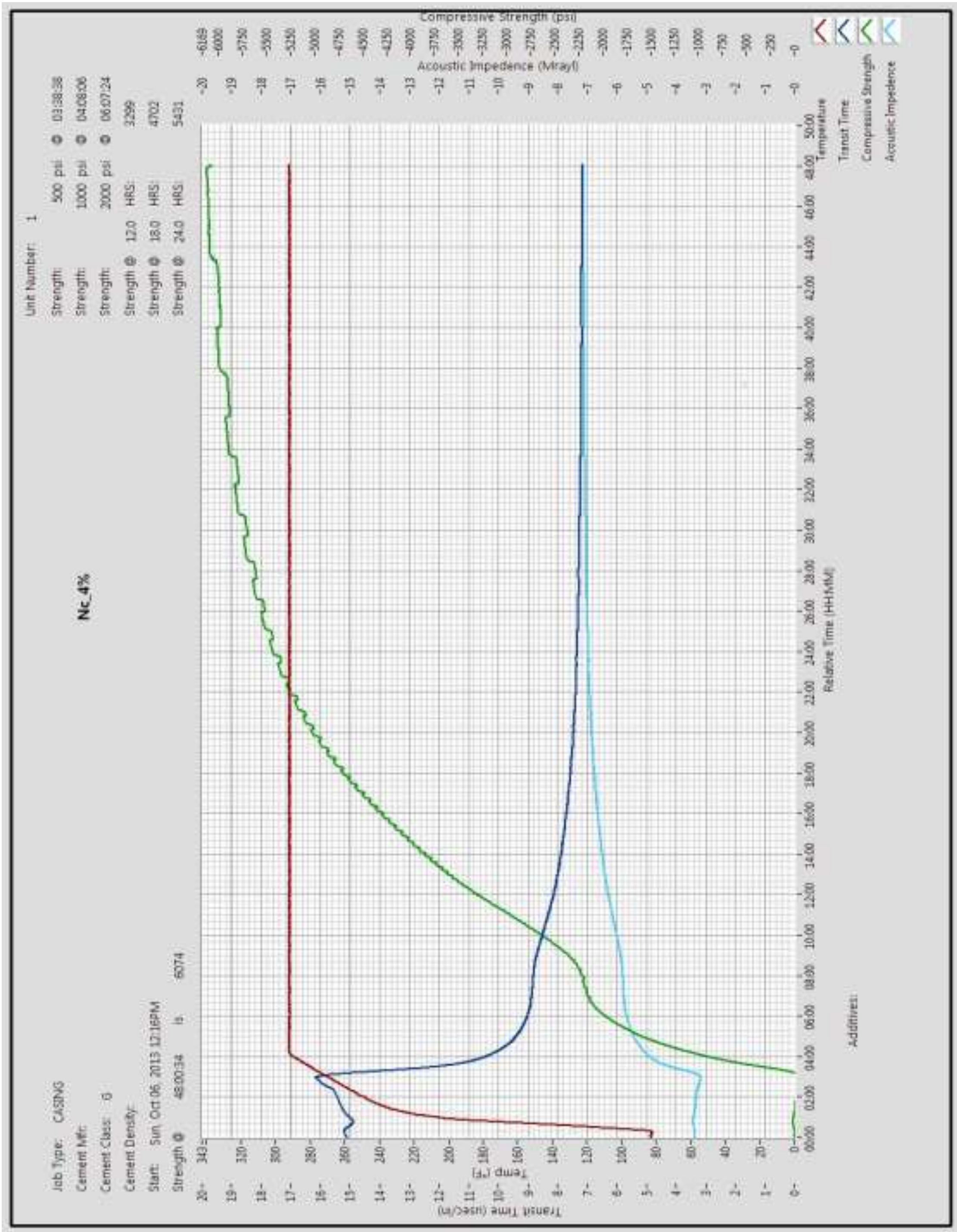

Figure 4.19: Compressive strength development of 4% Nano clay cement slurry at HPHT

To solve this strength retrogression problem in selected well, 35% BWOC silica flour has been added to the cement design to get the base slurry for this particular well. Later, different Nano clay percentages are mixed in base slurry to study the super mechanical potential of Nano clay as **Table 4.5** explains the compressive strength tests results. It is evident that addition of Nano clay resulted in high early compressive strength as shown in **Figure 4.15** and **Figure 4.16**. The 1% Nano clay cement system provides high compressive strength after 48 hours. The further addition resulted in low compressive strength as mentioned before; increasing in amount of Nano clay reduced the slurry density.

Table 4.5: Compressive strengths results (Psi) at different time durations (12, 18, 24& 48) hours

Time (HH:MM)	**Class G**	**Base Mix**	**1% NC**	**2% NC**	**3% NC**	**4% NC**	**2%NC + 0.5%NS**
12:00	2487	2833	2919	3048	3749	3299	3736
18:00	2698	5707	5844	5340	5229	4702	5229
24:00	2744	6467	6690	6206	6093	5431	6173
48:00	-	6812	7190	6550	6918	6074	-

Table 4.6: Time to gain compressive strengths (50,500 &2000 psi)

Compressive strength Psi	**Class G**	**Base Mix**	**1% NC**	**2% NC**	**3% NC**	**4% NC**	**2%NC & 0.5%NS**
	Time (HH:MM)						
50	01:25	03:33	03:34	03:29	03:40	03:38	03:50
500	01:58	04:00	04:00	03:54	04:04	04:08	04:03
2000	07:03	09:28	08:02	07:51	05:49	06:07	05:51

Table 4.6 represents the cement slurry development with time and focus on the time required for each cement system to develop a compressive strength of 50 Psi and 500 psi. These compressive strengths are considered sufficient enough to support the steel casing / liner prior to resuming the drilling operation. The transition period between developing a compressive strength of 50 psi and 500 psi is important and needed to be as short as possible to avoid long waiting time on cement before resuming drilling operation. Cement slurry of simple Class G cement has shortest time to attain the 500psi compressive strength as it gains the strength within 2 hours which shows its ability to set early. But Class G cement alone is not a good choice to inject in HPHT wells. The new cement system is designed according to selected well conditions as given in **Table3.1**.

After performing the tests on cement systems containing different percentages of Nano clay, it is investigated that cement system having Nano clay percentage of (3.0% BWOC) yielded in the shortest transition period (24 minutes) of gaining compressive strength from 50 psi to 500 psi while the cement slurry having Nano clay percentage of (0%), (1.0%), (2%) & (4%) yielded on transition periods of (27, 26, 25 & 30) minutes respectively with insignificant difference (see **Figure 4.20**).

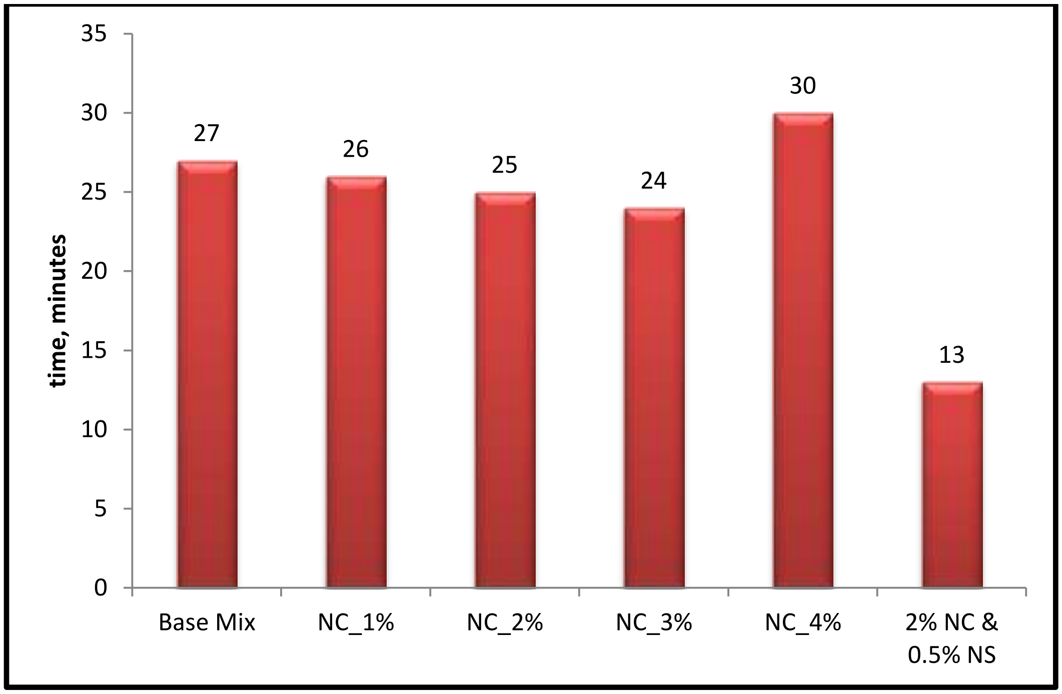

Figure 4.20: Transition time trend of achieving 50 to 500 psi compressive strength

Time to gain 2000psi compressive strength is important in case of perforations and stimulations. The 3% Nano clay cement system has the shortest time duration to gain 2000psi compressive strength (see **Figure 4.21**). The 3% Nano clay cement system has low compressive strength after 48 hours but it has advantage of gaining early compressive strengths.

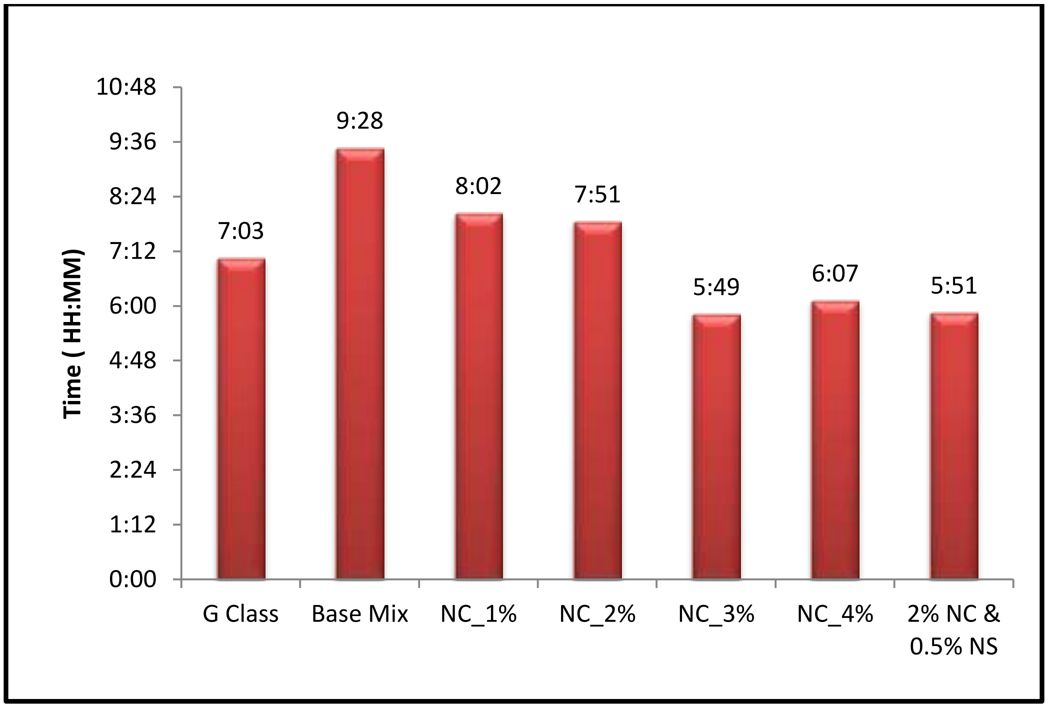

Figure 4.21: Time to gain 2000 psi compressive strength

Later a new mix was designed that consisted of both Nano clay and Nano silica with 2% and 0.5% BWOC respectively as the results are provided in **Table 4.5** and **Table 4.6**. The chart of this new mix is given in **Appendix A**. It is evident from the results that Nano clay and Nano silica admixed slurry improves the properties of cement and enhances the compressive strength of cement as compared to 3% Nano clay cement system. Their mixture reduces the time period of gaining 500Psi strength as compared to all Nano clay admixed slurries. But its behavior is almost similar with 3%BWOC Nano clay cement system as both systems compressive strengths are close to each other and the development of strength with time is quite similar. From the results, it is evident that Nano silica addition improves further properties of Nano clay mixed slurries and helps in fast development of compressive strength. The reason of this compressive strength development is high surface area and small particle size which helps fast hydration of cement.

Another mix of 3% Nano clay and simple class G has been tested and its results are given in Appendix A.

4.6.2 Effect of Nano Clay on Destructive Compressive Strength

The compressive strength properties determine the integrity of cement and its ability to bear long term imposed stresses (Adam, 1986). The four cement systems having Nano clay percentages of (0 %, 1.0 %, 2.0 % and 3%) and class G cement have been subjected to the API compressive strength test in which the moulds of cement are made and cured at 290°F and 3000 psi pressure for 24 hours in HPHT curing machine. At the end of test, the cubes are removed from moulds and crushed to get compressive strength.

From **Table 4.7** results, it is obvious that cement system having 1% Nano clay has higher compressive strength as compared to other cement systems. It is found that the addition of Nano clay by 1% BWOC increases compressive strength. But the further addition of Nano clay causes low compressive strengths (see Figure **4.22**). This low compressive strength results as the consequence of low density; as further addition of Nano clay as mentioned before lessen the density. Later, 3% Nano clay cement mix is subjected to compressive strength and observed that it does not affect the compressive strength appreciably. So, 2% and 3% BWOC Nano clay are not suitable mixing percentages in terms of strength as it reduced the compressive strength rather than to upturn it.

This high compressive strength is resulted from small size particles of Nano clay which fill the pores and make strong structure. Another reason was the high percentage availability of silica which provided more pozzolanic reaction which in result gave high compressive strength.

The base mix was repeated with different WCR and observed that water contents affected the compressive strength as shown in Table **4.8**. As the WCR is increased, it results in low compressive strength as compared to low WCR mix.

Later compressive strength test was conducted on different mixture mixed by different methods of mixing and concluded that the mixing process affected the compressive strength of cement. Dry mix, additives were blended in cement, has high compressive strength as compared to wet mix in which additives are mixed in water as obvious from the results (**Table 4.9**).

Similarly, 1% Nano silica cement slurry was subjected to compressive strength test and it was observed that addition of Nano silica resulted in high compressive strength as compared to base mix. From the comparison of Nano silica and Nano clay, it is obvious that 1% Nano silica and 1% Nano clay give similar results.

Table 4.7: Effect of Nano clay on the compressive strength of cement cured for 24hours at HPHT

Sample	**Class G**	**Base Mix**	**1% NS**	**1% NC**	**2% NC**	**3% NC**
1	3377.2	6045.7	6525	6927.81	5106.9	6259.2
2	3197.2	6748	6815	7388.62	5624.55	5438.9
3	3230.6	6130	7293.5	6585.17	5524.5	-
Average, psi	3268.3	6307.8	6877.8	6967.20	5418.65	5849.1

Table 4.8: Effect of WCR on compressive strength

WCR, %	**Base Mix, Psi**
43.5	7463.6
44	6307.8

Table 4.9: Effect of different methods of mixing on compressive strength

	1% Nano silica	
	Dry Mix	**Wet Mix**
	7395	6525
	8555	6815
	7554.5	7293.5
Average, psi	7811.9	6878

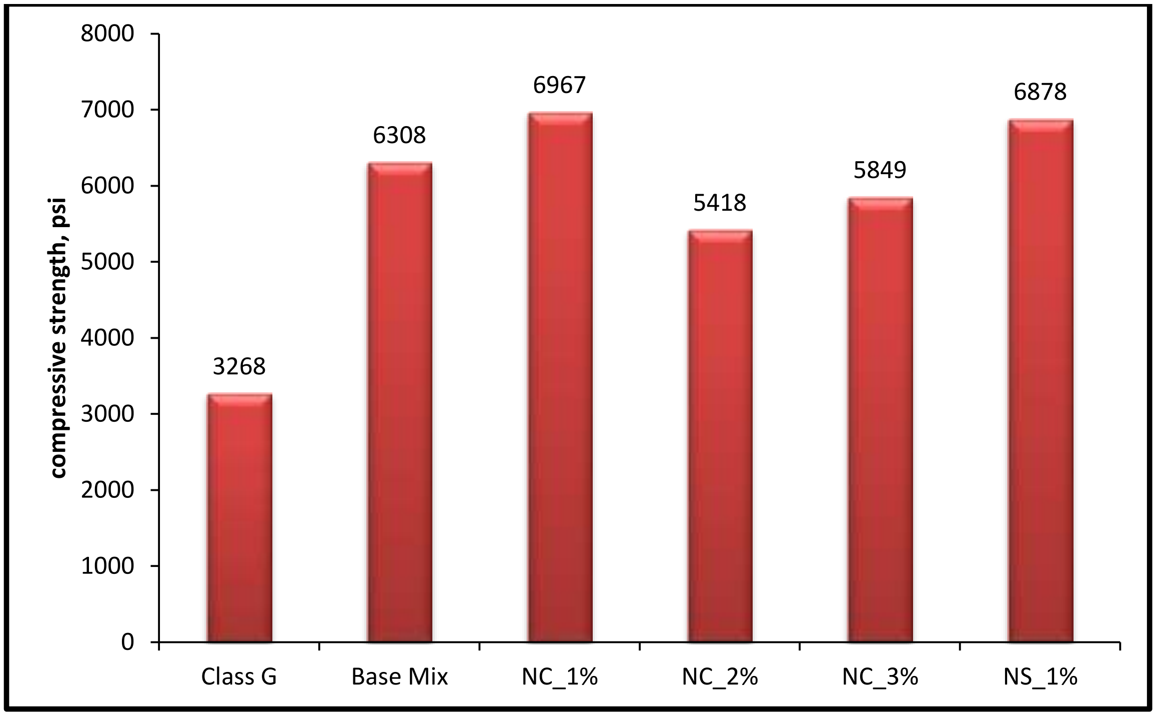

Figure 4.22: Compressive strength trend by crushing method

4.6.3 Effect of Nano Clay on Compressive Strength at Ambient Condition

The method which employed to determine the cement compressive strength, direct method by applying physical forces to square inch cement cubes.

The cube moulds of cement are made and conditioned for a day at 25°C and atmospheric pressure. The cubes are removed from moulds and kept in water for next 2 days. At the end of curing period, the cubes crushed to get compressive strength. The **Table 4.10** explains the results of compressive strength for different percentages of Nano Clay conducted at ambient conditions.

Table 4.10: Crushing compressive strength results of Nano clay mix cured at ambient conditions for 3 days

Slurry Type	Nano Clay Percentage (%BWOC)	Compressive Strength Psi
S1	1	2972
S2	2	3502
S3	3	2645

From the **Table 4.10** results, it is obvious that addition of Nano clay to cement system affects the compressive strength of cement. The rise in percentage of Nano clay results in increase of the compressive strength.

For the ambient tests, coarse silica was used instead of fine silica flour. For the mixing of 3% BWOC Nano clay cement slurry, the dispersant percentage was increased from 0.4% to 1% BWOC for easy mix. But in other cement systems, the dispersant percentage was kept low about 0.4%BWOC. From the experiment results, it is investigated that 2% BWOC Nano clay cement system has high compressive strength as compared to 1% and 3% Nano clay cement system. The cement system having 3%BWOC Nano clay gives lower compressive strength which is because of high percentage of dispersant and low density. As the dispersant percentage is increased, the compressive strength is also reduced in 3%BWOC Nano clay cement system as it is evident from **Figure 4.23** compressive strength trend with respect to different percentages of Nano clay.

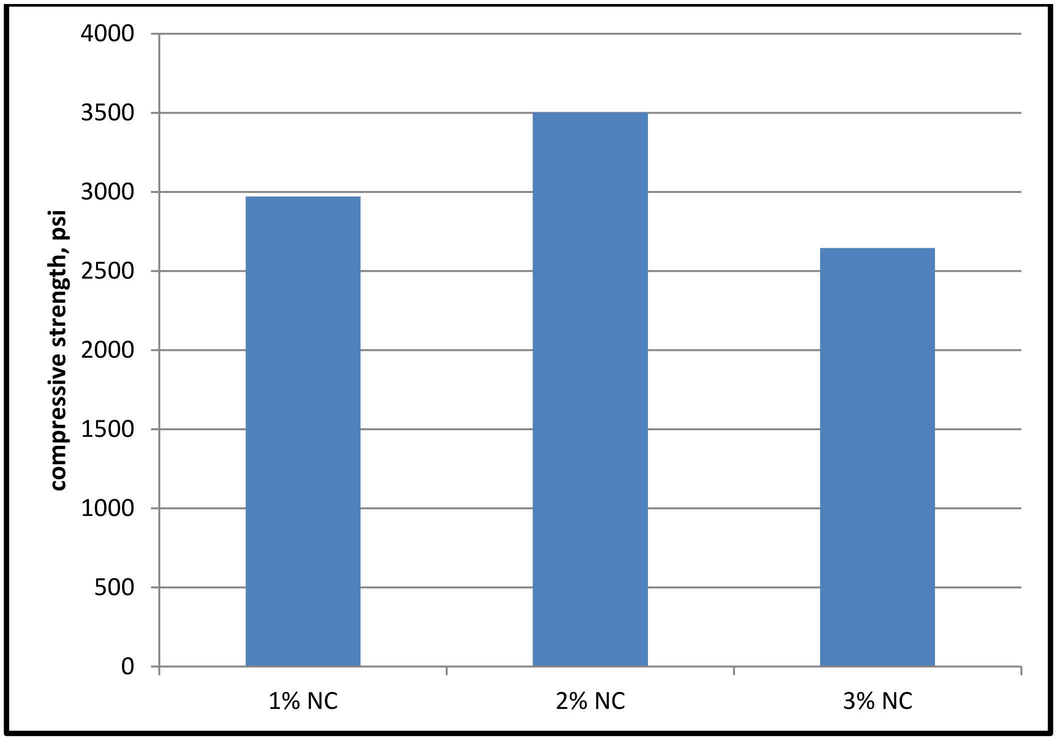

Figure 4.23: Effect of Nano clay on compressive strength at ambient conditions

4.7 Effect of Nano Clay on Porosity and Permeability

Permeability determines the ability of fluid to flow at different pressure and helps in determining the long term performance of cement. As the cement sheath is supposed to seal the zones and prevents fluid migration. This is only possible if we have low permeability.

In this test, cement plugs have been drilled out of cubes of cement and conducted the permeability and porosity tests on the automated porosimeter/permeameter at 500psi confining pressure.

Table 4.11 explains Nano clay effects on the permeability and porosity of cement after curing at 24 hours. In new formulated slurries, the Nano clay mix makes non uniform particle distribution which results in reduction of porosity and permeability of slurries. When simple class G cement is subjected to high temperature and pressure conditions, it results in high porosity and permeability results. This behavior of Class G causes low integrity and high gas migration problem. Later cement slurry designed without Nano clay was subjected to such extreme conditions and it resulted in low permeability and porosity. The addition of Nano clay by 1% BWOC results further reduction in the permeability and porosity. Further upturn in Nano clay percentage by 2% and 3% result in high permeability. As already mentioned that increasing the Nano clay percentage, lessened the density; thus permeability of slurries increased (see Figure **4.25**). Another reason of this rise in permeability with addition of Nano clay is the particle size and high surface area of Nano clay. Nano clay being smaller size particles trapped more air on its surface which later results in high permeability of cement.

The behavior of porosity is a little different from permeability as it can be investigated that the porosity decreases up to the addition of 2% Nano clay in mix with minute change in it but further addition causes rise in porosity (Figure **4.24**).

Table 4.11: Porosity and permeability of Nano clay (0, 1, 2& 3) % cement systems after 24 hours of curing

Parameters	**G class**	**Base Mix**	**1%NC**	**2%NC**	**3%NC**
Permeability md	0.358	0.0041	0.001	0.0035	0.0064
Porosity,%	36	31	28.35	27.2	29

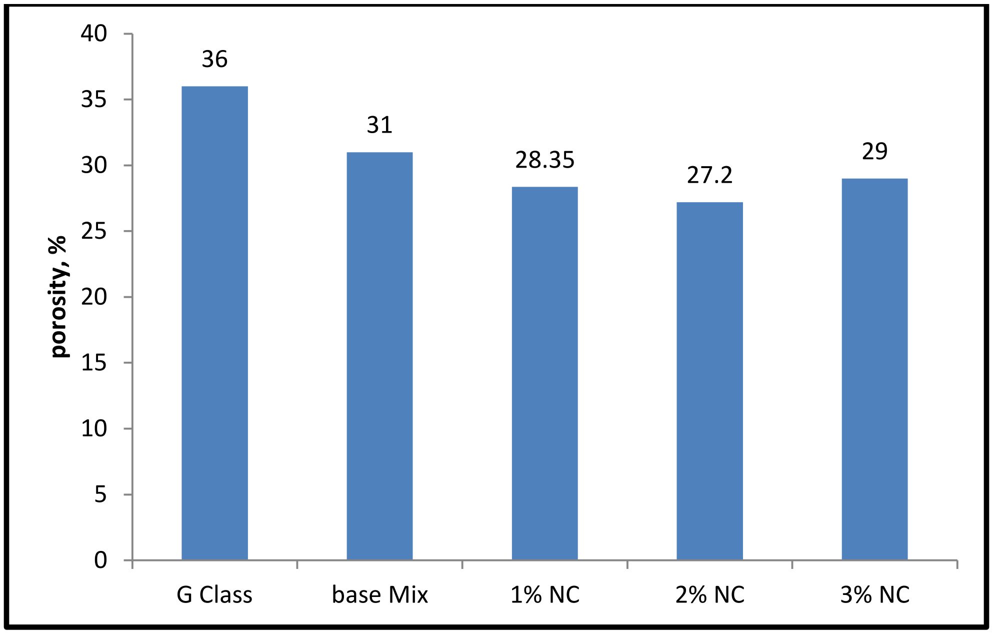

Figure 4.24: Porosity trend of Nano clay admixed slurries

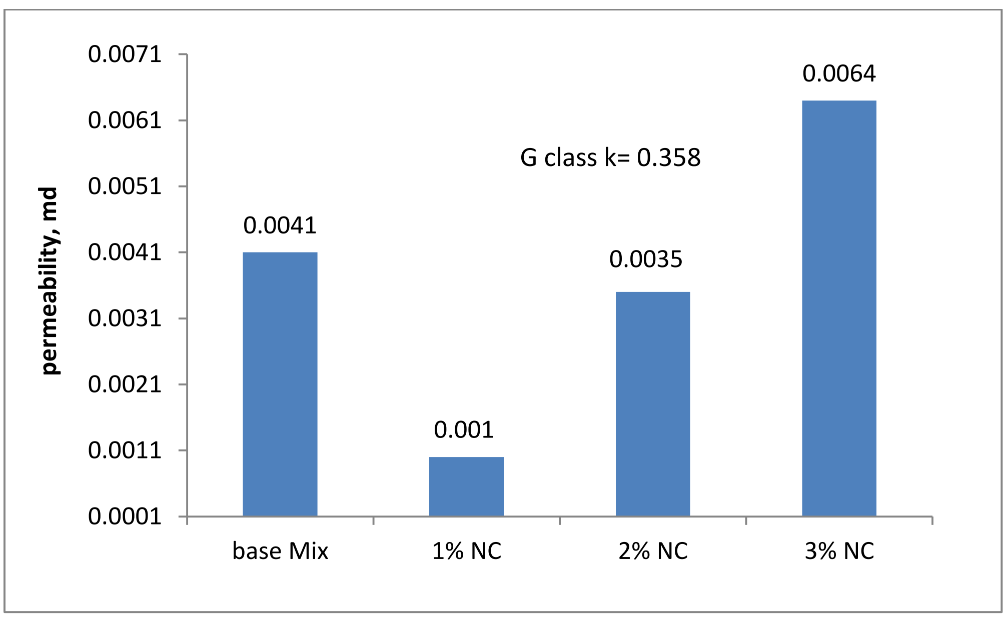

Figure 4.25: Permeability trend of Nano clay admixed slurries

Later, Nano silica slurry was subjected to permeability and porosity tests. It was investigated that addition of 1%BWOC Nano silica provided low permeability and porosity (see **Table 4.12**). The non-uniform distribution of small particles helps in filling the small capillaries which indirectly reduce the permeability and porosity.

Table 4.12: Porosity and permeability of 1% Nano silica admixed cement system

Parameters	Base Mix	1%NS
Permeability, md	0.0041	0.0026
Porosity,%	31	27.1

4.8 Microstructural Analysis

The microstructure of cement slurry is studied using both SEM and XRD analysis. SEM explains the composition and pore structure. While XRD is well-known techniques for studying cement composition and hydration.

The hydration products of Class G oilwell cement mainly depend on the curing temperature. The results indicated that the major hydration products of clean cement slurry are calcium silicate hydrate gel CSH (II) [$Ca_2SiO_4 \cdot 3H_2O$], C_2SH_2[$Ca_2SiO_4 \cdot 2H_2O$], $C_3S_2H_3 \cdot$ [$Ca_3(HSiO_4)2 \cdot 2H_2O$], calcium hydroxide CH[$Ca(OH)_2$], ettringite Aft [$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$] and monosulphate Afm [$3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$].

The XRD patterns of neat class G cement slurry hardening paste under low and higher temperatures are given **Figure 4.26** and **Figure 4.27** respectively.

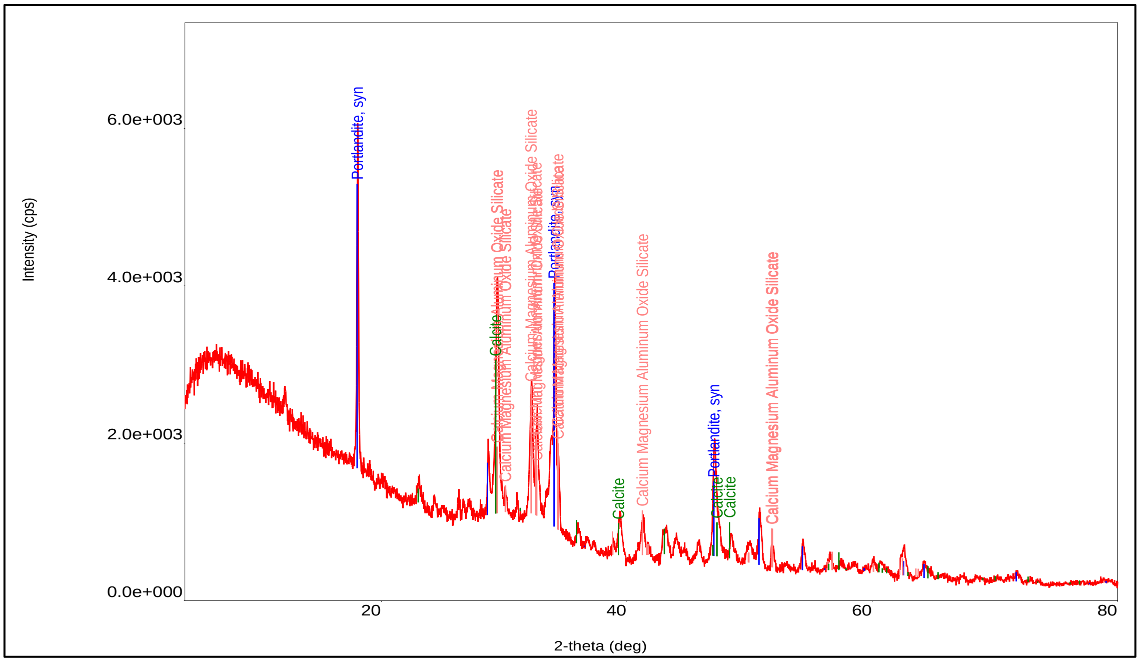

Figure 4.26: XRD spectra of G type cement after 8 hours hydration at ambient conditions

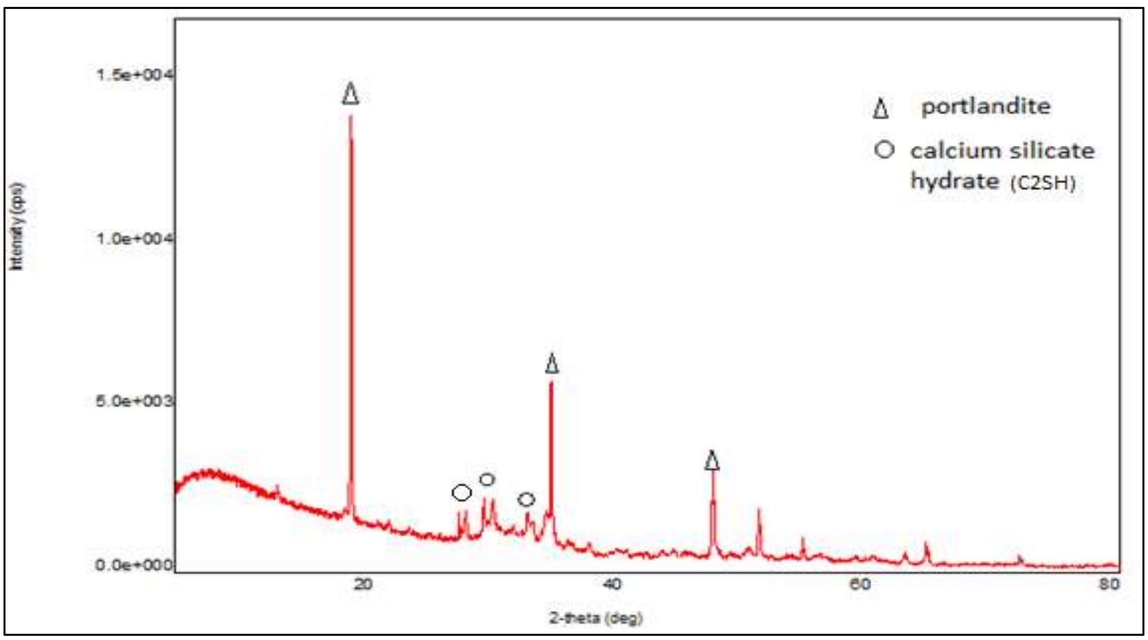

Figure 4.27: XRD spectra of G type cement after 24 hours hydration at HPHT conditions

It is evident that hydration of cement at low temperature leads to formation of portlandite (CH) and calcium silicate hydrate (CSH) which is not detected at low temperature hydration because of amorphous behavior at low conditions.

When the curing temperature exceeded 110 ℃, the products CSH (Ⅱ) began to be transformed into C_2SH [$Ca_2SiO_4 \cdot H_2O$] called α-dicalcium silicate hydrate. Under these conditions, there was no difference between the product compositions for different temperatures, but the amount of each product could vary with curing temperature because there were slight differences in the peak intensity for the XRD pattern of different curing temperatures. With the increase of curing temperature, di-poly-silicate hydration products began to increase. The analysis given above indicates that the major products of Class G oilwell cement were CH and CSH(Ⅱ) when curing at low temperature conditions.

CSH (Ⅱ) is a fiber-shaped, in which the fiber can branch at every 0.5 μm length during the growth of the particle. The branches of these particles adhere to each other and form a continuous three-dimensional network in the hardened paste (see **Figure 4.28**). Thus, when the curing temperature is below 110 ℃, the major hydration products mentioned above could adhere to each other to give the hardened paste with obvious characteristics of a network structure. But when the curing temperature exceeded 110 ℃, with the products being transformed into the high crystallinity product C_2SH, which is in the shape of a plate-block, the microstructure of the hardened paste was also transformed from a fiber network into the morphology of a pile of plate-blocks (see **Figure 4.30**). Since C_2SH is a very weak and porous matter, and the bonding stress between these big block crystals is weak, the structural stress of hardened paste would partially concentrate and increase, the compressive strength would decrease to some extent. With the increase of curing temperature, the crystalline grain of C_2SH became much larger, and many mass blocks were piled up in the hardened paste.

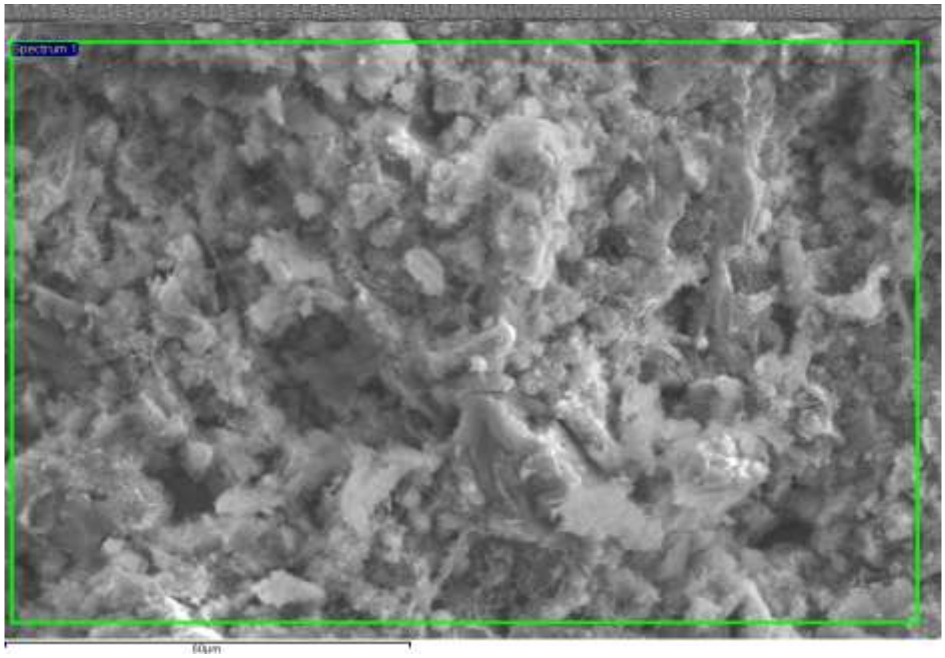

Figure 4.28: SEM of hydration products of simple class G cement cured at normal conditions for 8 hours

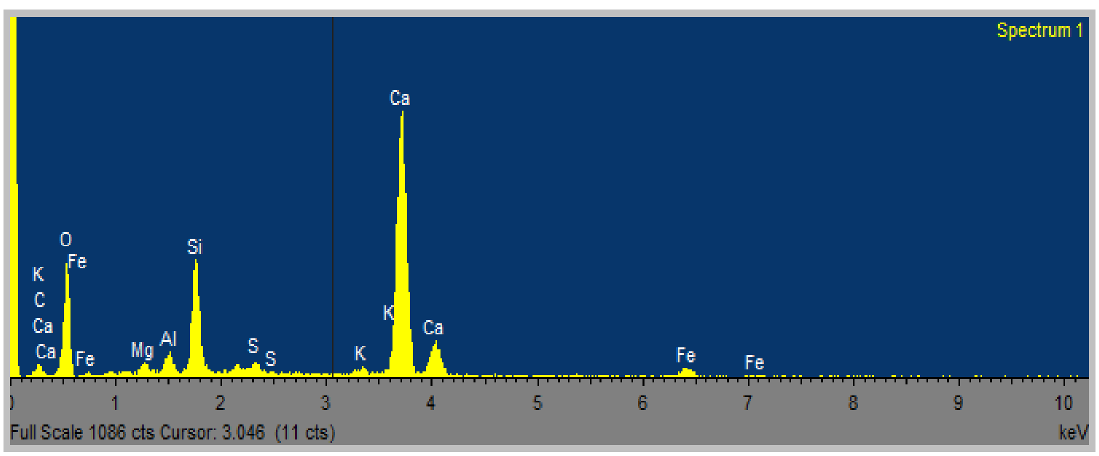

Figure 4.29: EDX of hydration products of simple class G cement cured at normal conditions for 8 hours

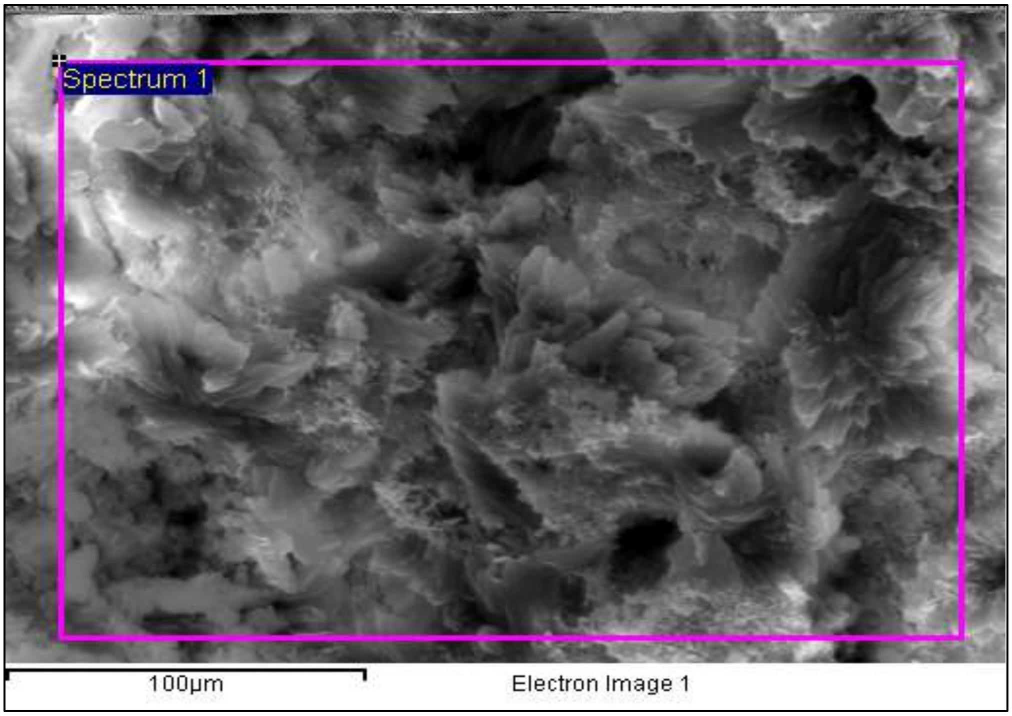

Figure 4.30: SEM of hydration products of simple class G cement cured at high conditions (144°C) for 24 hours

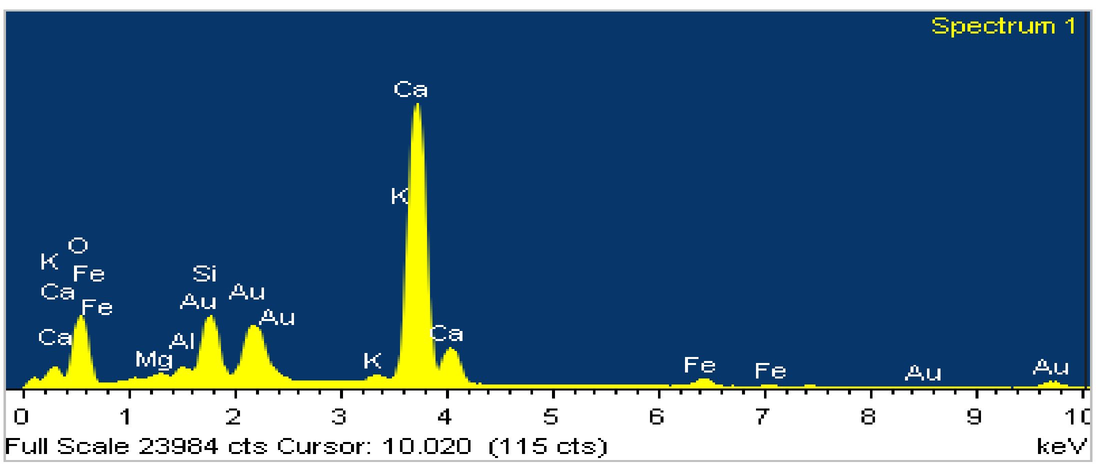

Figure 4.31: EDX of hydration products of simple class G cement cured at HPHT for 24 hours

When 35% BWOC of silica flour was added to the cement slurry, the hydration products were totally different from clean slurry under the curing condition of 144 °C, 3000 psi and 1 day. There were obvious specific peaks of SiO_2 in the XRD patterns. But the specific peaks of CH weakened with the increase of the amount of silica flour.

The specific peaks of CH and C_2SH almost disappeared in the hydration products when 35% silica flour was added to the cement slurry. This indicates that a great amount of C_2SH had been transformed into $C_5S_6H_5$ (tobormorite). Under this condition, there still were specific peaks of SiO_2 in the XRD pattern (see **Figure 4.32**).

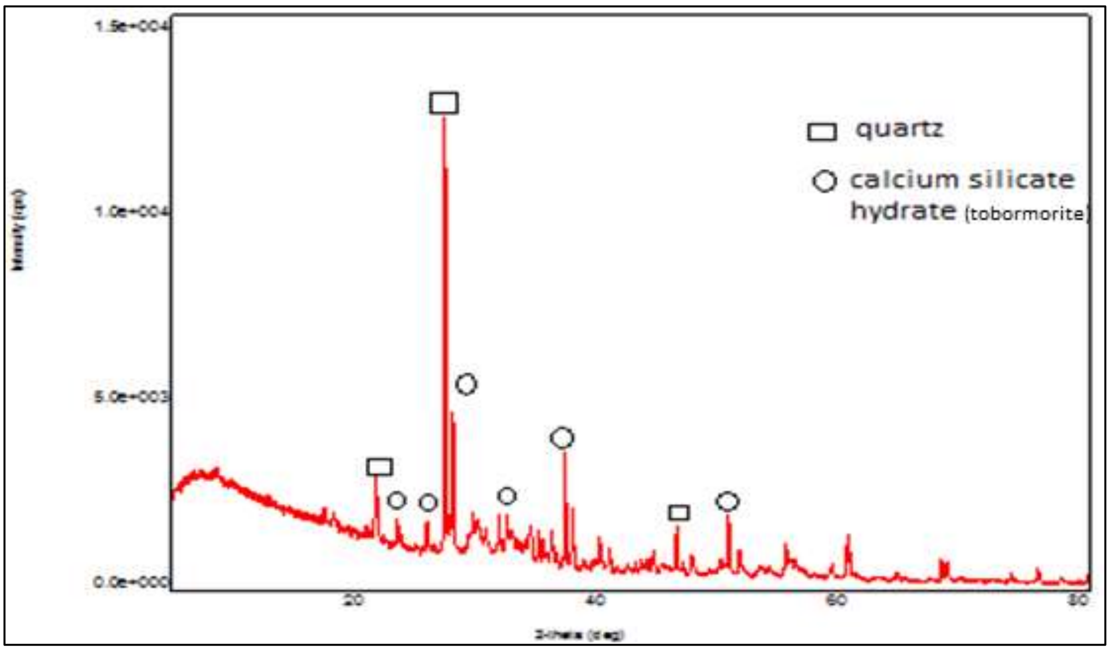

Figure 4.32: XRD spectra of hydration products containing 0% Nano clay cured at HPHT conditions for 24 hours

In cement slurry with silica flour, $C_5S_6H_5$ could be produced during hydration and it was a kind of good crystal with needle shape. These needle shape of $C_5S_6H_5$ products could interweave and join each other to build an ideal and well-proportioned network structure in hardened paste (see **Figure 4.33**). So set cement could retain a high compressive strength.

Even from the EDX (**Figure 4.34**) it is evident that CSH percentage is quite high after the hydration of cement cured at HPHT conditions

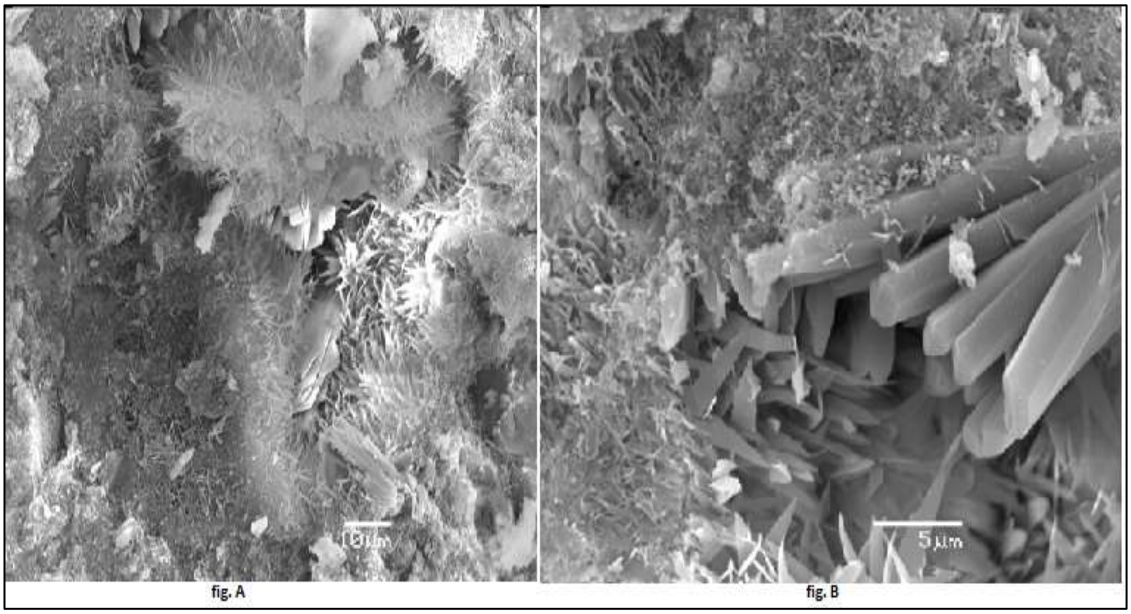

Figure 4.33: SEM photographs of hydration products of 0% Nano clay cement slurry cured at HPHT conditions for 24 hours

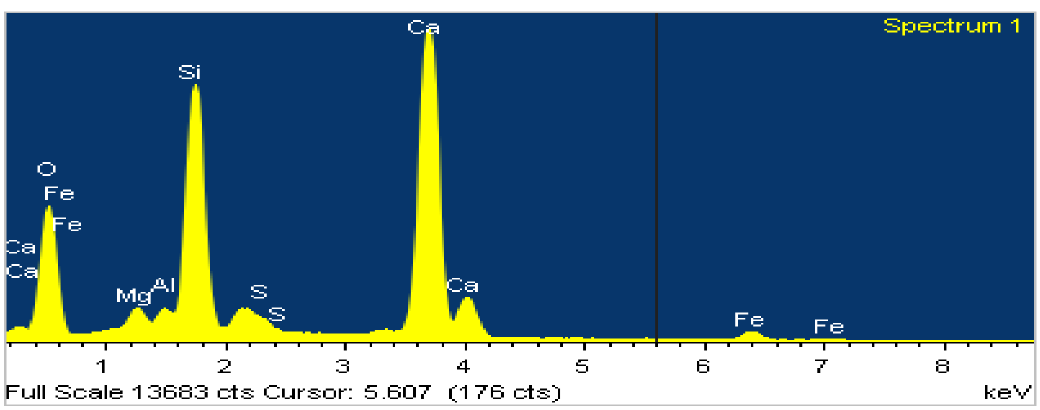

Figure 4.34: EDX of hydration products of 0% Nano clay cement slurry cured at HPHT conditions for 24 hours

As the Nano clay was incorporated in the mix, it formed more polymerization and least CH appeared in the mix. The smaller particle size and greater surface area reacted with

CH in solution to produce more CSH. Less CH was available for diffraction. The 1% Nano clay, when mixed in base cement, it made strong structure and resulted in formation of quartz and CSH in high percentage. The CSH is detected in XRD diffraction (see **Figure 4.35**).

In cement slurry with Nano clay, highly dense CSH is produced due to high availability of silica, and it was a kind of good crystal that provides high compressive strength. These crystal products could interweave and join each other to build an ideal and well-proportioned network structure in hardened paste (see **Figure 4.36**). The small size of Nano clay helps in filling the capillaries and resulted in dense structure. So set cement could retain a high compressive strength.

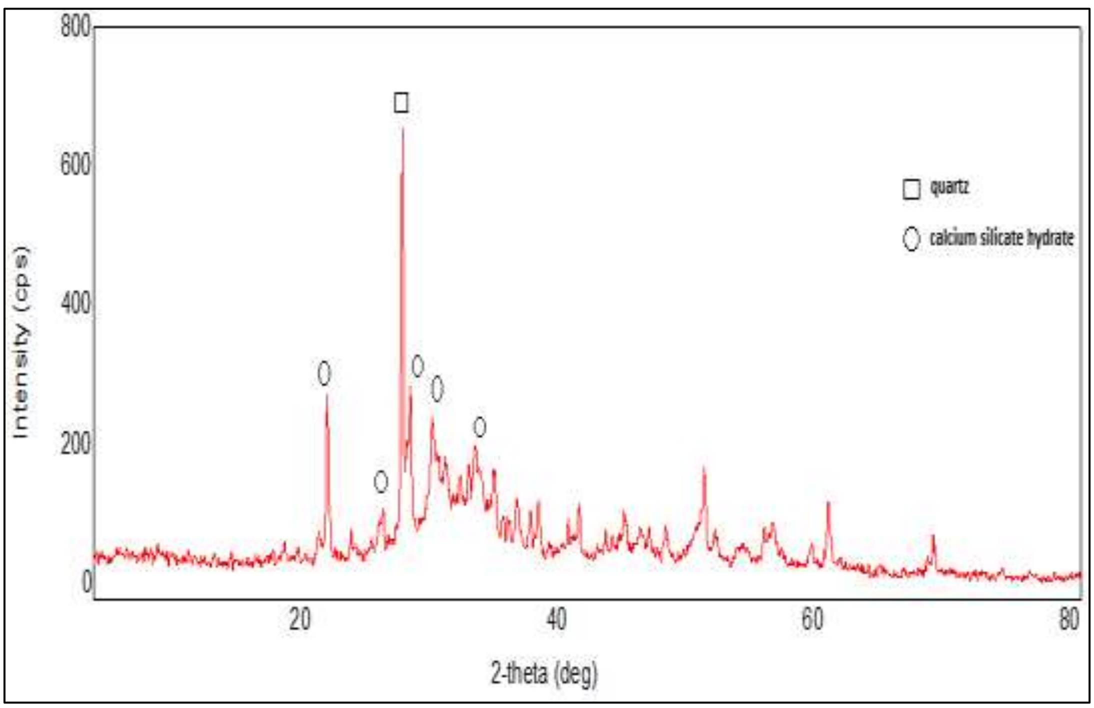

Figure 4.35: XRD of hydration products of 1% Nano clay cement slurry cured at HPHT conditions for 24 hours

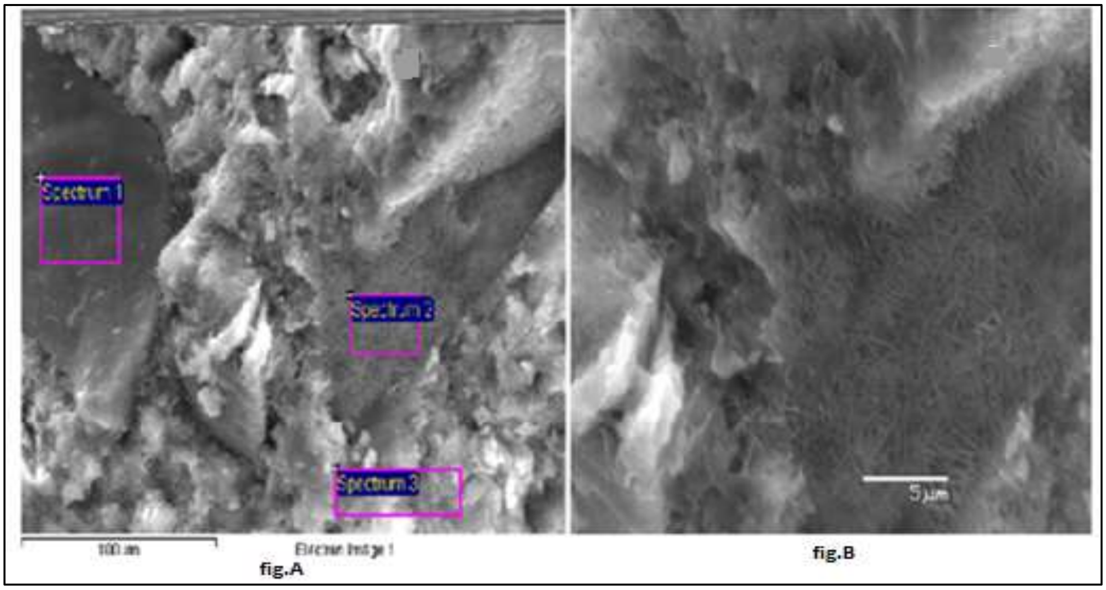

Figure 4.36: SEM photographs of hydration products of 1% Nano clay cement slurry cured at HPHT conditions for 24 hours

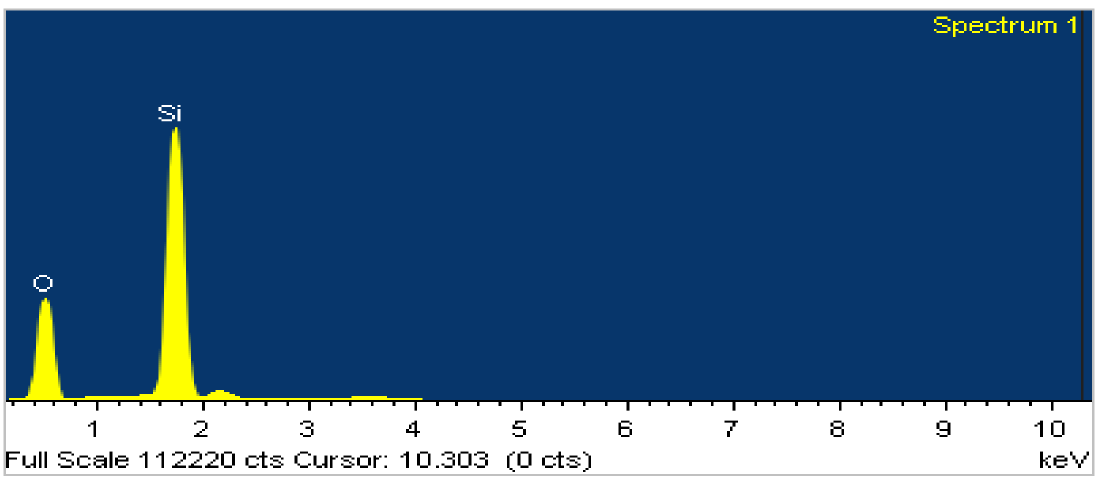

Figure 4.37: EDX of hydration products of 1% Nano clay cement slurry

During the hydration of cement slurry with Nano clay by 2%, high percent of quartz (SiO_2) could be produced during hydration with CSH due to high availability of silica (see **Figure 4.38**). These crystals of SiO_2 products could interweave and join each other to build an ideal and well-proportioned network structure in hardened paste

(**Figure 4.39**). The quartz effect on compressive strength is not noticeable as evident that 2% Nano clay cement system gives low strength compared to 1% Nano clay system.

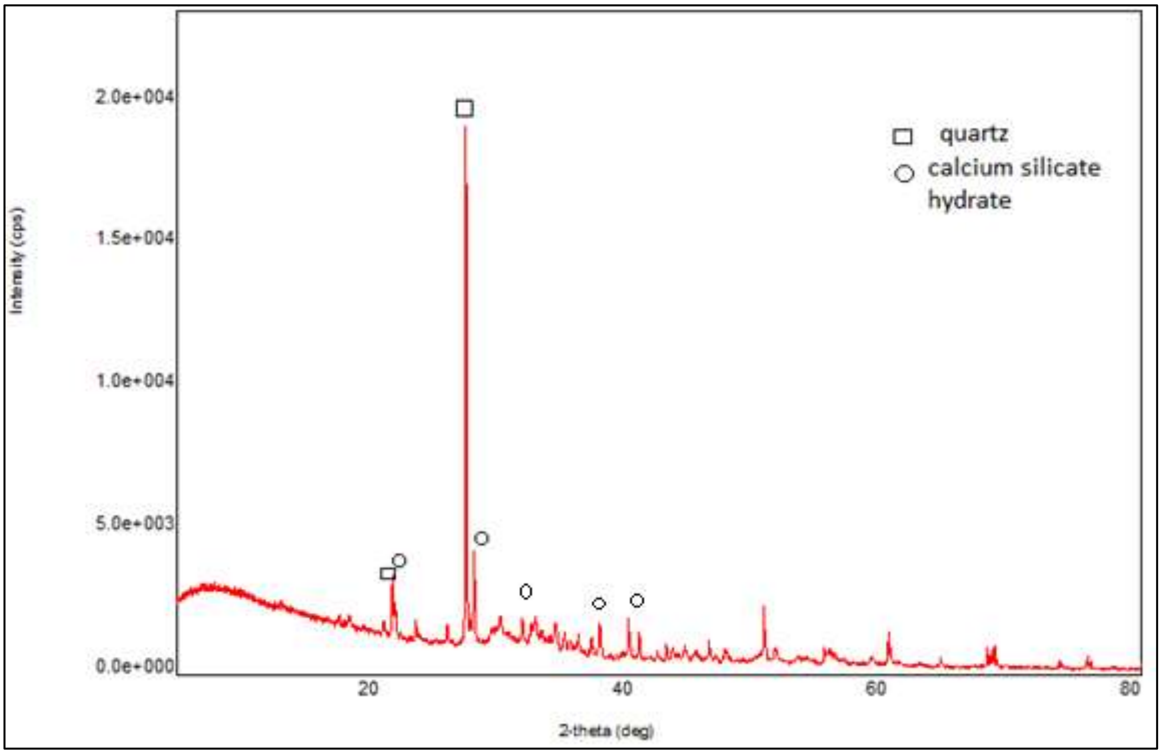

Figure 4.38: XRD of hydration products of 2% Nano clay cement slurry cured at HPHT conditions for 24 hours

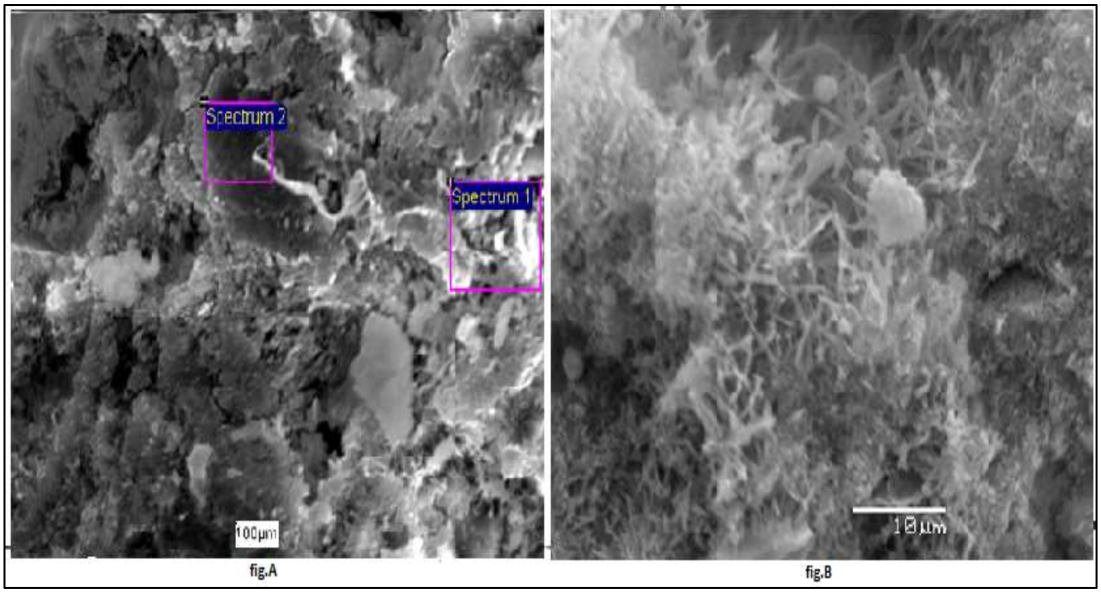

Figure 4.39: SEM photographs of hydration products of 2% Nano clay cement slurry cured at HPHT conditions for 24 hours

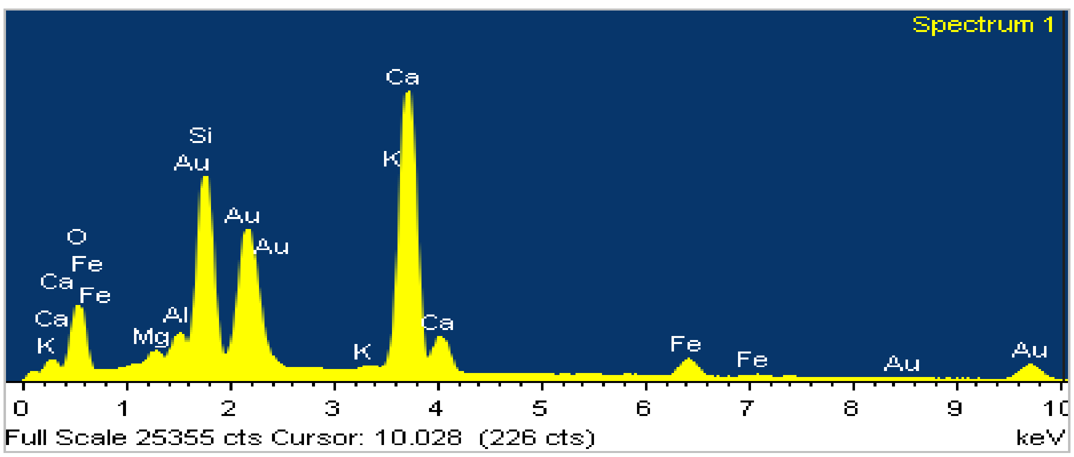

Figure 4.40: EDX of hydration products of 2% Nano clay cement slurry

As the Nano clay was added by 3% BWOC in cement slurry, it helped in more pozzolanic reaction and formed a dense structure of tobormorite crsytals which usually formed in presence of high silica and contributes in compressive strength (**Figure 4.41**). From the SEM analysis, it can be observed that there are some voids appeared in the structure (see **Figure 4.42**). The EDX explains the high percentage of calcium and silica in the cement that shows the formation of CSH in the cement mix after 24 hours of hydration (see **Figure 4.43**).

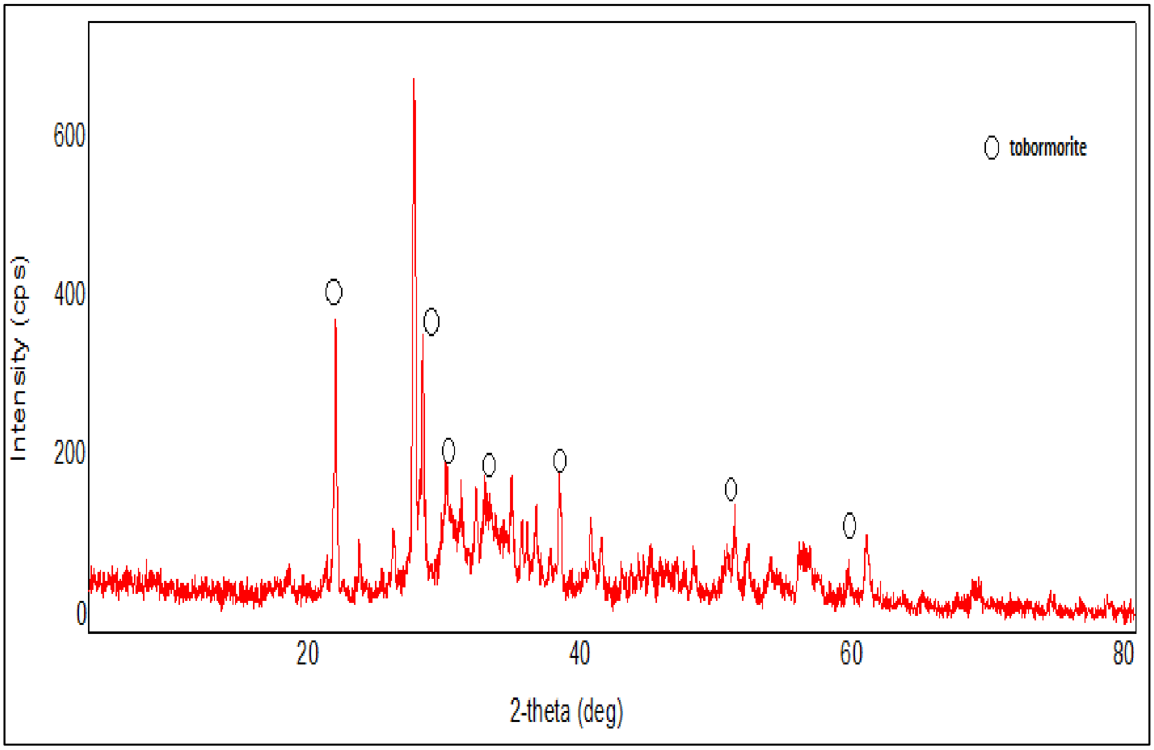

Figure 4.41: XRD of hydration products of 3% Nano clay cement slurry cured at HPHT conditions for 24 hours

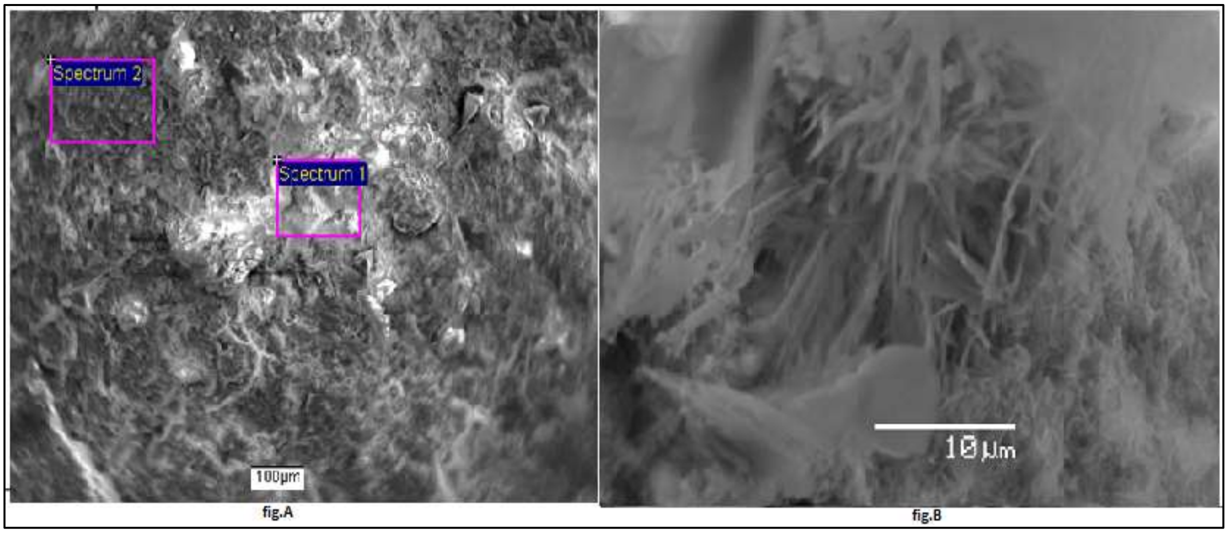

Figure 4.42: SEM photographs of hydration products of 3% Nano clay cement slurry cured at HPHT conditions for 24 hours

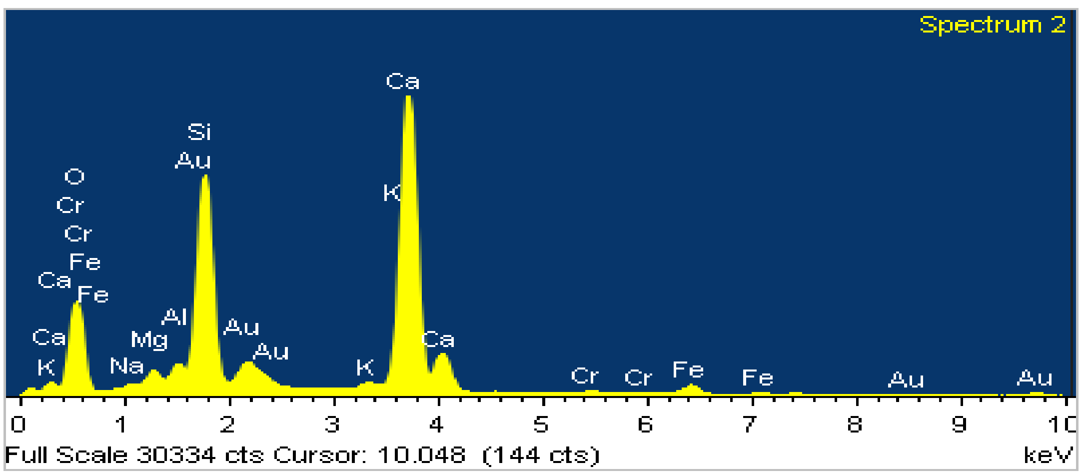

Figure 4.43: EDX of hydration products of 3% Nano clay cement slurry

For the analyzing the effects hydration of Nano silica, 1% BWOC Nano silica was added in cement slurry. The development of CSH was improved as the CH was mostly converted to CSH in the presence of high percentage of silica. This phenomenon captured in **Figure 4.44**, the change of CH percentage for the mixes that contained Nano silica packages. The cement mix which had the smallest Nano silica and a large distribution had the least CH. This concept refers back to the greater surface area well graded size distribution can cover and react with, compared to a narrow distribution of sizes. As it is observed that the smaller particle size and greater surface area reacted with CH in solution to produce more CSH. Less CH was available for diffraction.

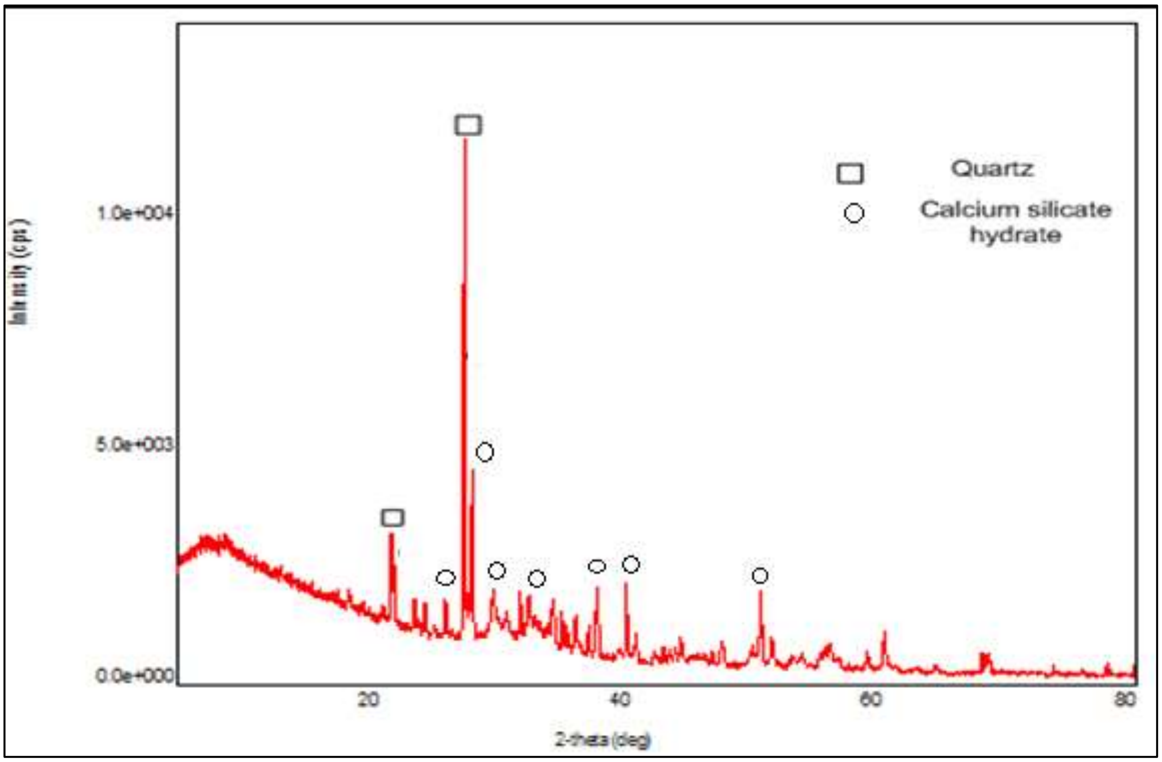

Figure 4.44: XRD of hydration products of 1% Nano silica cement slurry cured at HPHT conditions for 24 hours

As the Nano silica was added in cement slurry, the CH concentration is transformed into CSH in more organized form (see **Figure 4.45**). The form of CSH in the presence of Nano silica is more stable as compared to mix without of it. The quartz crystals were appeared in the mix which showed the high polymerization of silica as it is obvious from the EDX (see **Figure 4.46**).

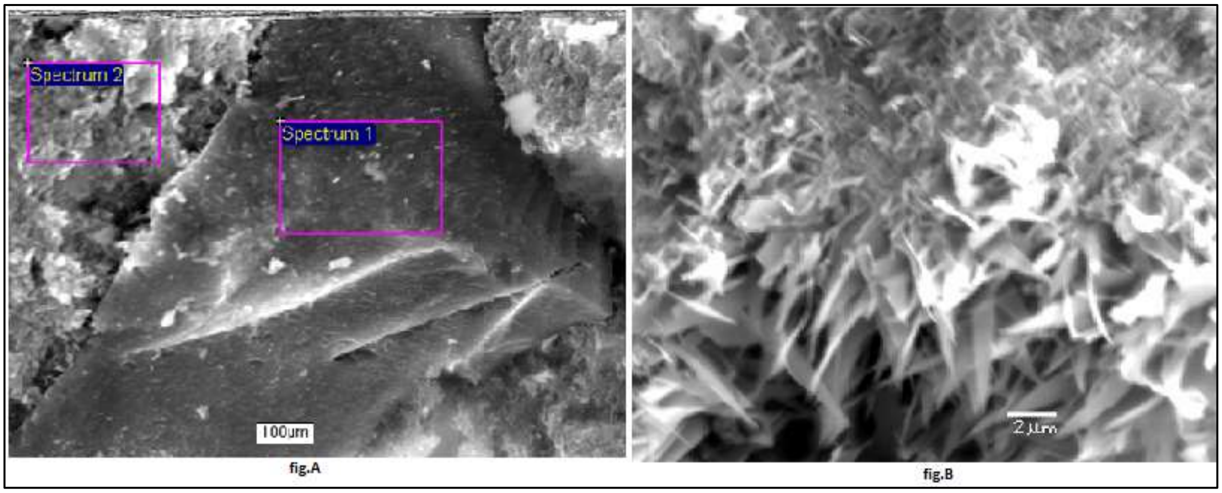

Figure 4.45: SEM photographs of hydration products of 1% Nano silica cement slurry cured at HPHT conditions for 24 hours

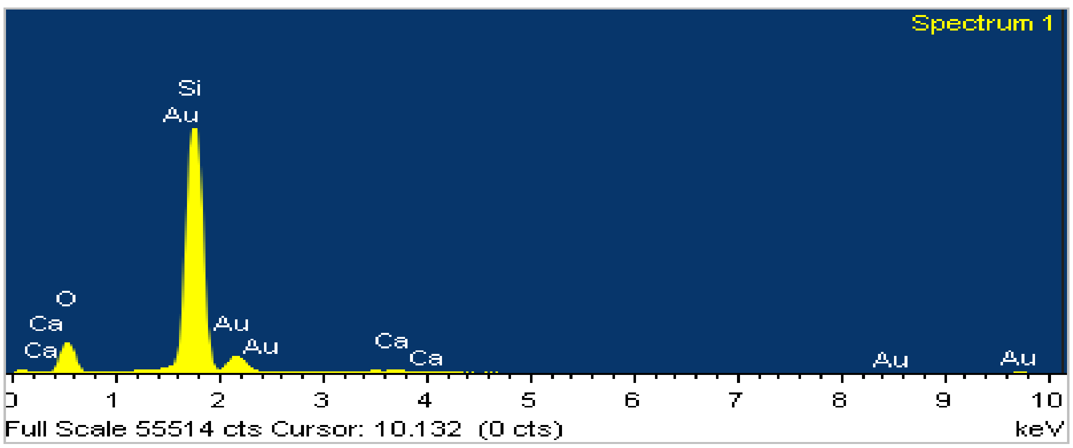

Figure 4.46: EDX of hydration products of 1% Nano silica cement slurry

Later, the hydration and microstructural analysis of samples after 48 hours of curing were performed and their results are provided in **Appendix B and C.**

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

This thesis is directed to assess the effect of Nano clay on Portland Saudi cement type 'G' in high pressure and temperature cementing applications. Tests required to characterize the performance of cement with Nano clay have been conducted under HPHT conditions. Thickening time, free water separation, slurry density, rheological properties, compressive strengths and porosity and permeability tests have been conducted.

The results of this study are restricted to the selected well conditions, cement used, chemical additives, percentages of Nano clay, and cement slurry preparation and testing procedures. This study would be useful for researchers interested in this area and would provide valuable information for the enhancement of state of the art Nano clay in cement.

5.1 Conclusions

The drilling and completion of a well is a capital project that needs to be accomplished properly. As a consequence, a detailed design is required, taking into consideration all loads that may affect the integrity of a well throughout its life span.

The findings of this investigation highlight the importance of Nano clay in cement design. Conclusions made from the research are summarized as follows;

1) From thickening time test, it is observed that Nano clay acts as a retarder as it slows down the hydration reaction. So, it may help in very deep well cementing.

2) There is no free water separation in all Nano clay cement systems after aging as Nano clay blocks the capillaries and prevents the water flow.
3) It is observed that addition of Nano clay reduces the density of cement slurries. But the difference in densities of all Nano clay cement systems is minimal.
4) From the rheology test, it is investigated that Nano clay addition increases the viscosity and yield point of cement slurry. This behavior makes the Nano clay viscosifier which helps in mud displacement.
5) From the compressive strength by sonic method, it was investigated that addition of Nano clay by 1% BWOC resulted in high early compressive strength. The further addition resulted in low compressive strength as mentioned before; increasing Nano clay amount, lessen the density of slurry.
6) From the compressive strength by destructive method, it was evaluated that addition of Nano clay by 1% provides high compressive strength.
7) From the permeability and porosity investigations, it can be concluded that Nano clay addition decreases permeability and porosity. In conventional design, the particles are distributed uniformly but in this particular design with Nano clay, the particles distribution is non-uniform. So, they resulted in low permeability and porosity. The 1% Nano clay cement system provides low permeability and 2% Nano clay results in low porosity.
8) From the microstructural analysis, it is obvious that small particles of Nano clay fill the pores and block the capillaries in the cement. In result, they provide the dense cement structure.

9) XRD analysis of cement mix with Nano clay shows that the addition of Nano clay transforms the CH phase to calcium silicate hydrate and tobermorite at high temperature which prevents strength retrogression and gives low permeability to the cement.

10) The mixture of both Nano clay and Nano silica provides good compressive strength and fast hydration.

5.2 Recommendations

This work includes the findings of Nano clay effects on oilwell cement properties in high pressure and temperature applications but still a lot of work left to be done. In all experiments, the behavior of Nano clay with other silica products has been investigated. But there is a need to investigate the effect of Nano clay in the absence of other silica products. The impact of Nano clay effects in shallow applications with low pressure and temperature conditions and with different water to cement ratios should be investigated.

Nano clay and Nano silica have potential to provide high integrity to cement sheath in high temperature applications separately. Different combinations of both materials should be designed and investigated their effects on oilwell cement properties. The impact of other Nano materials including Nano alumina, Carbon Nano tubes and Nano Fe_2O_3 should be investigated.

Appendix A: Compressive Strength by Sonic Method

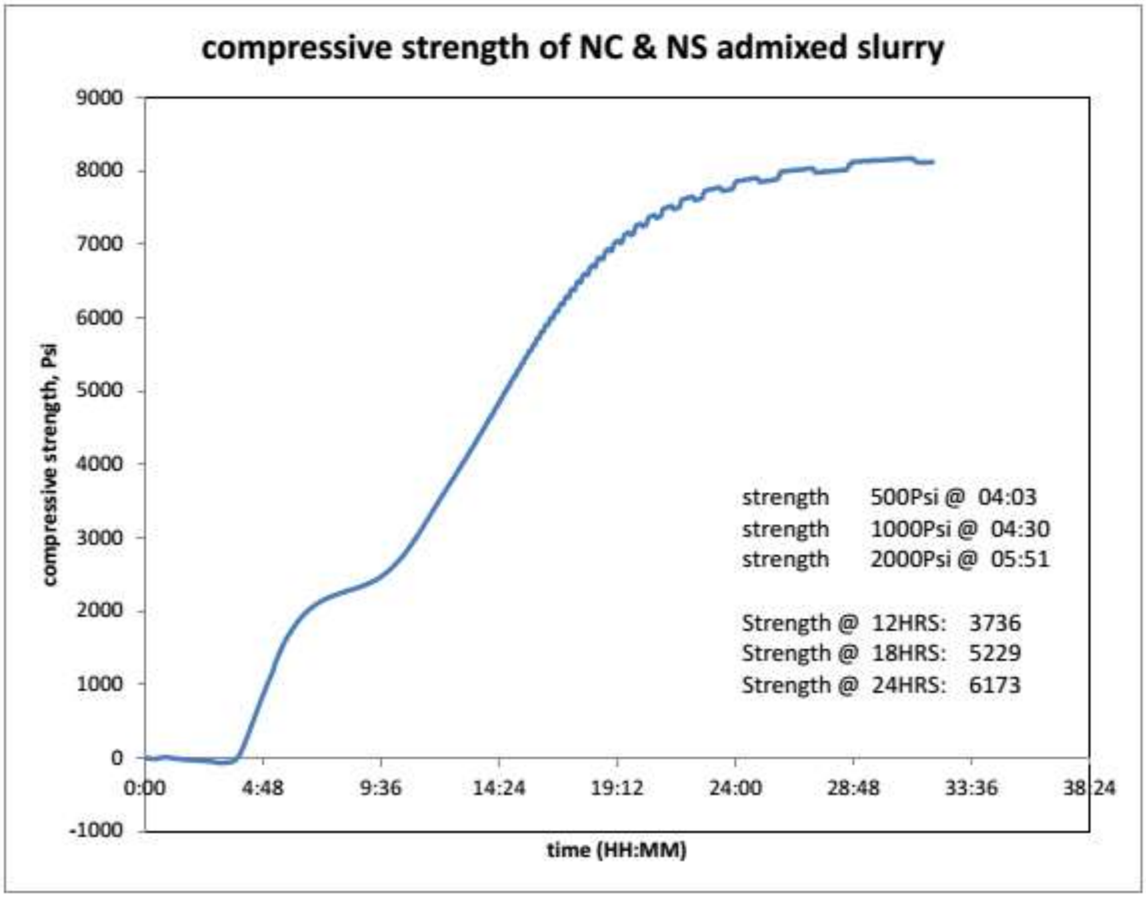

Figure A 1: Compressive strength of Nano clay (2%) and Nano silica (0.5%) admixed slurry

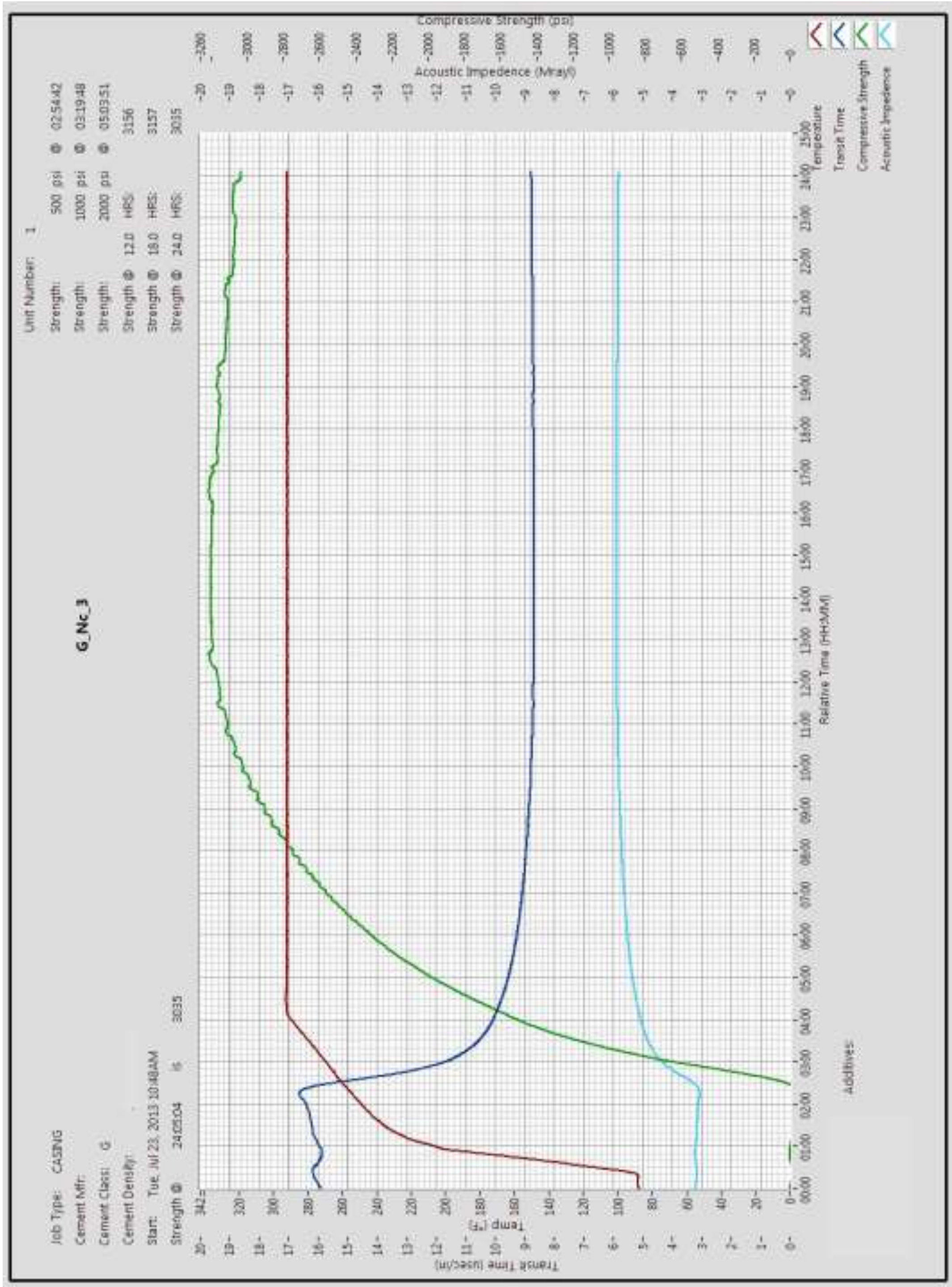

Figure A 2: Compressive strength of 3% Nano clay and simple class G cement mix slurry

Appendix B: XRD plots of (0, 1, 2, 3) % Nano clay slurries cured at 48 hours

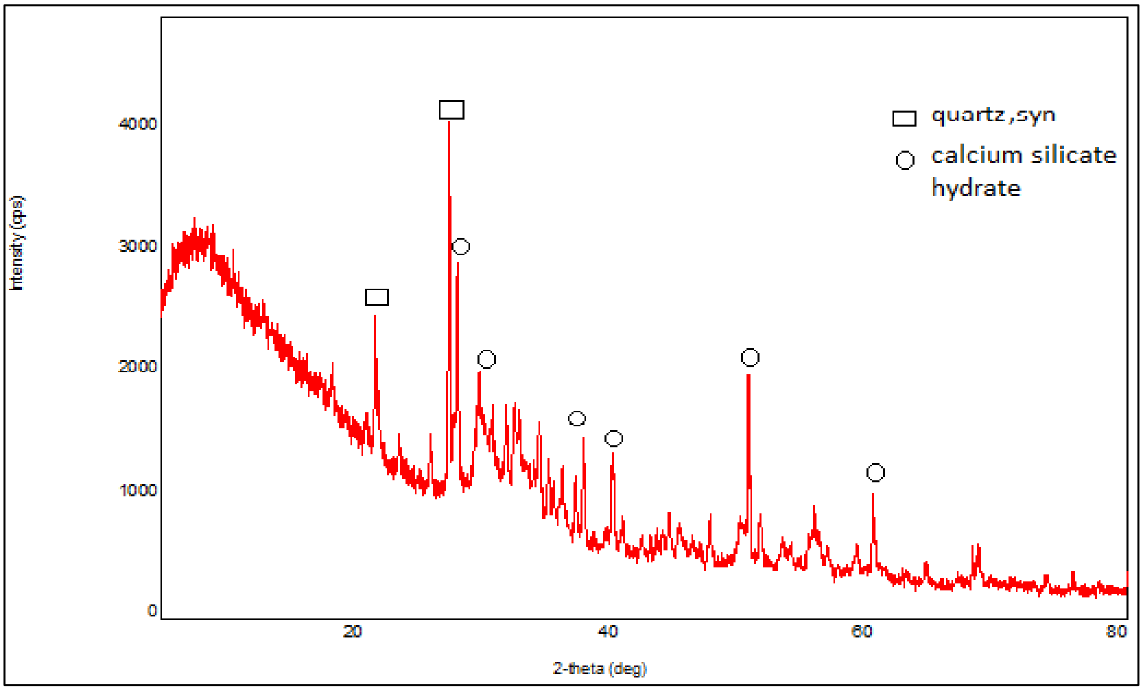

Figure B 1: XRD plot of 0% Nano clay mixed slurry after curing 48 hours

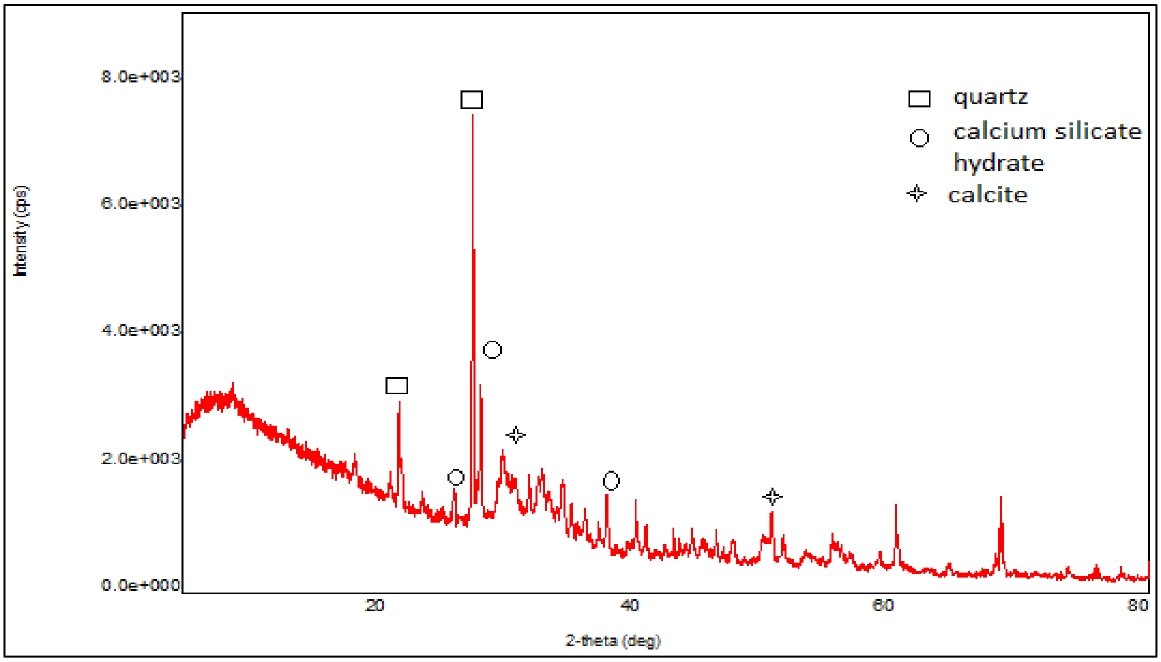

Figure B 2: XRD plot of 1% Nano clay mixed slurry cured for 48 hours

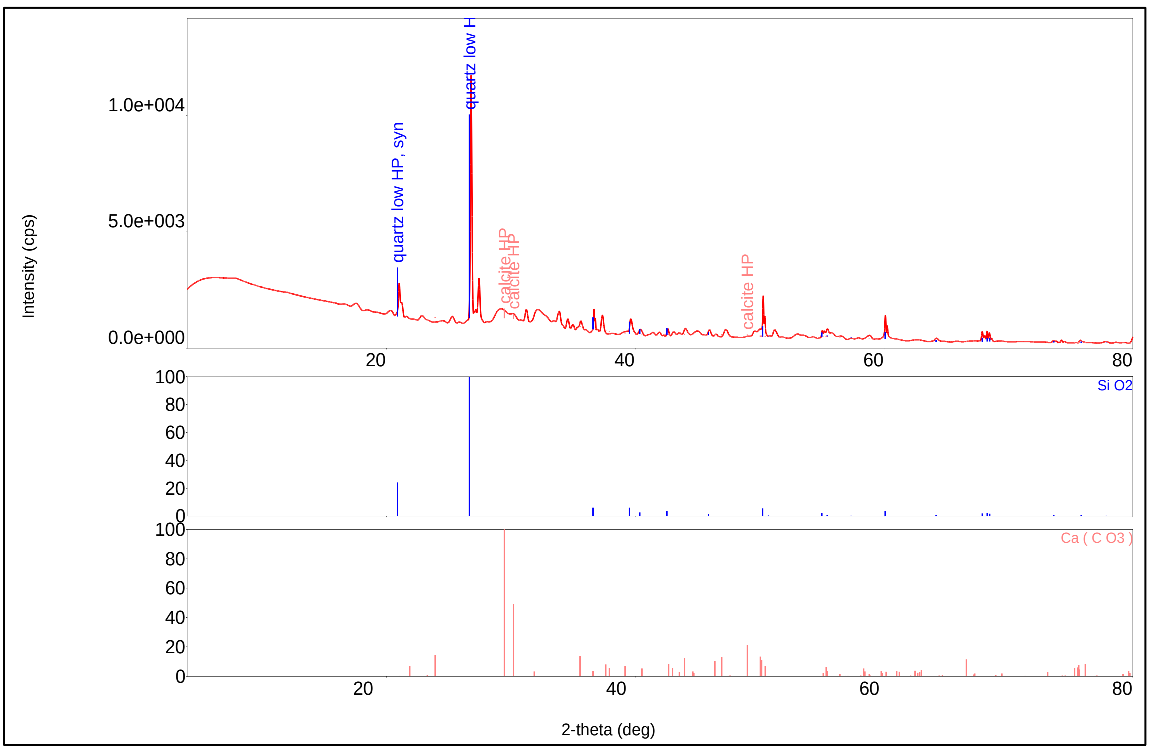

Figure B 3: XRD plot of 2% Nano clay mixed slurry cured for 48 hours

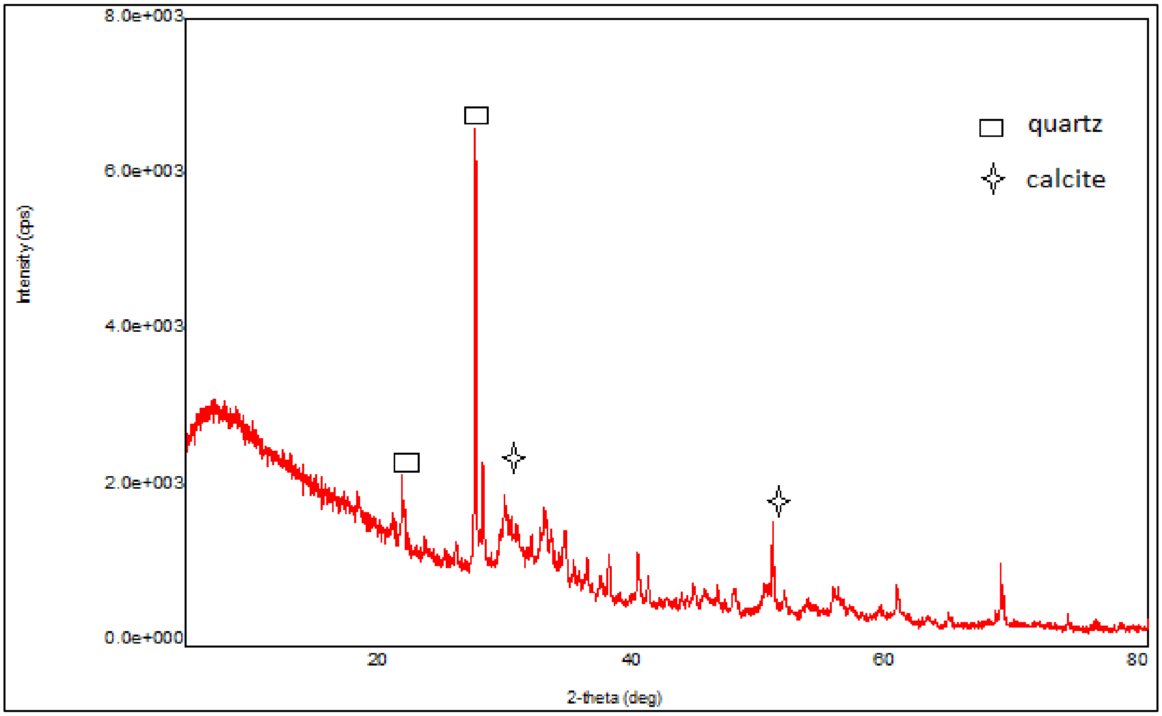

Figure B 4: XRD plot of 3% Nano clay mixed slurry cured for 48 hours

Appendix C: SEM images of cement systems containing (0, 1, 2, 3) % Nano Clay

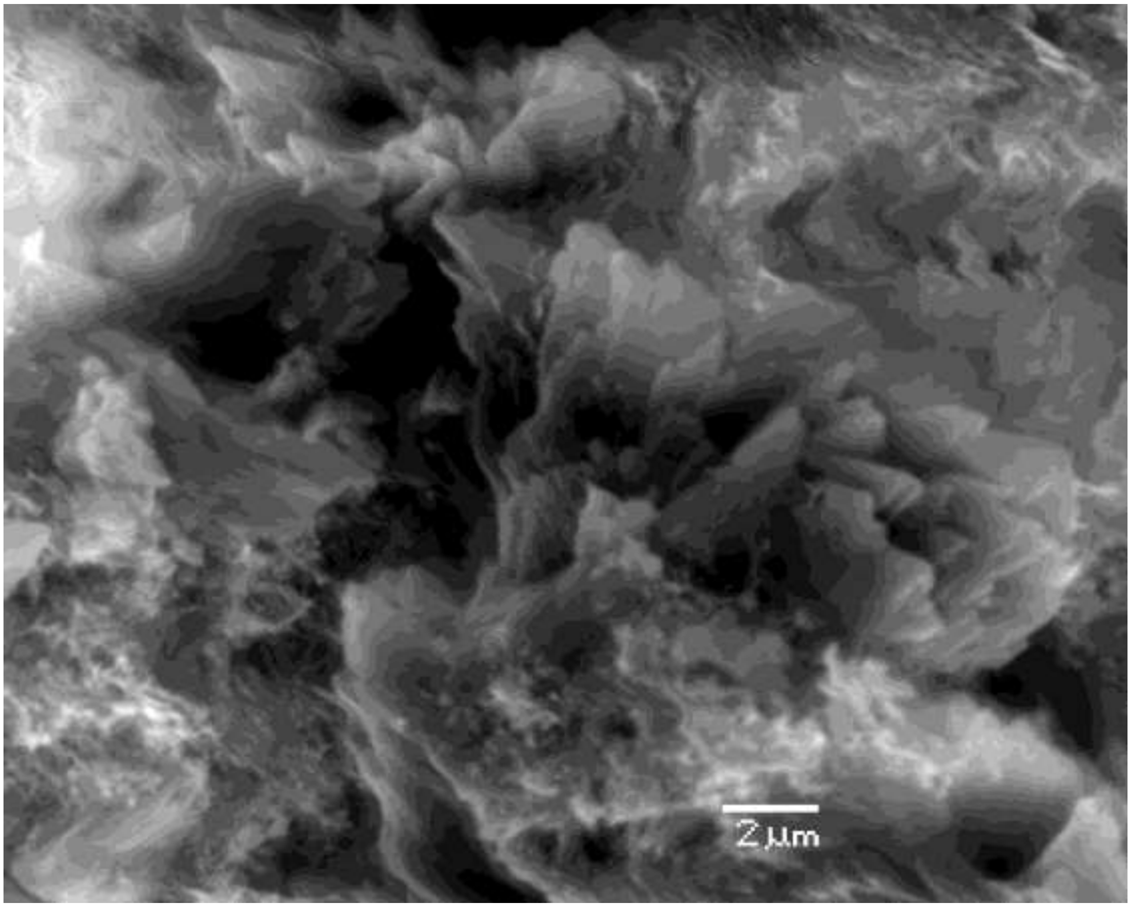

Figure C 1: SEM of simple G class slurry cured at HPHT for 24 hours

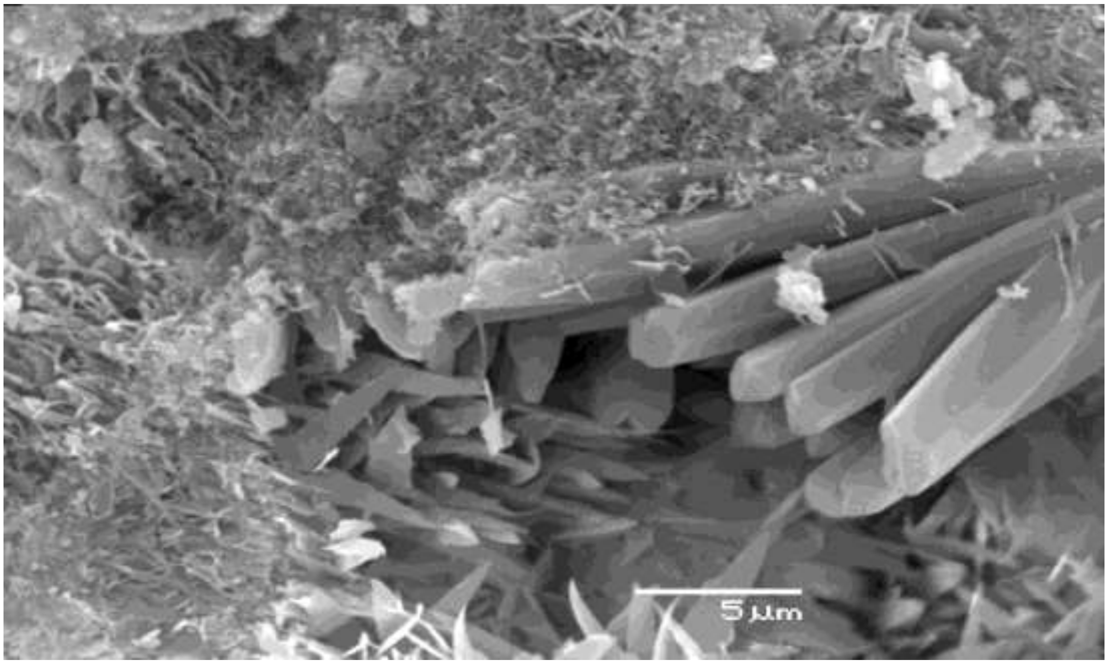

Figure C 2: SEM of 0% Nano clay mixed slurry cured at HPHT for 24 hours

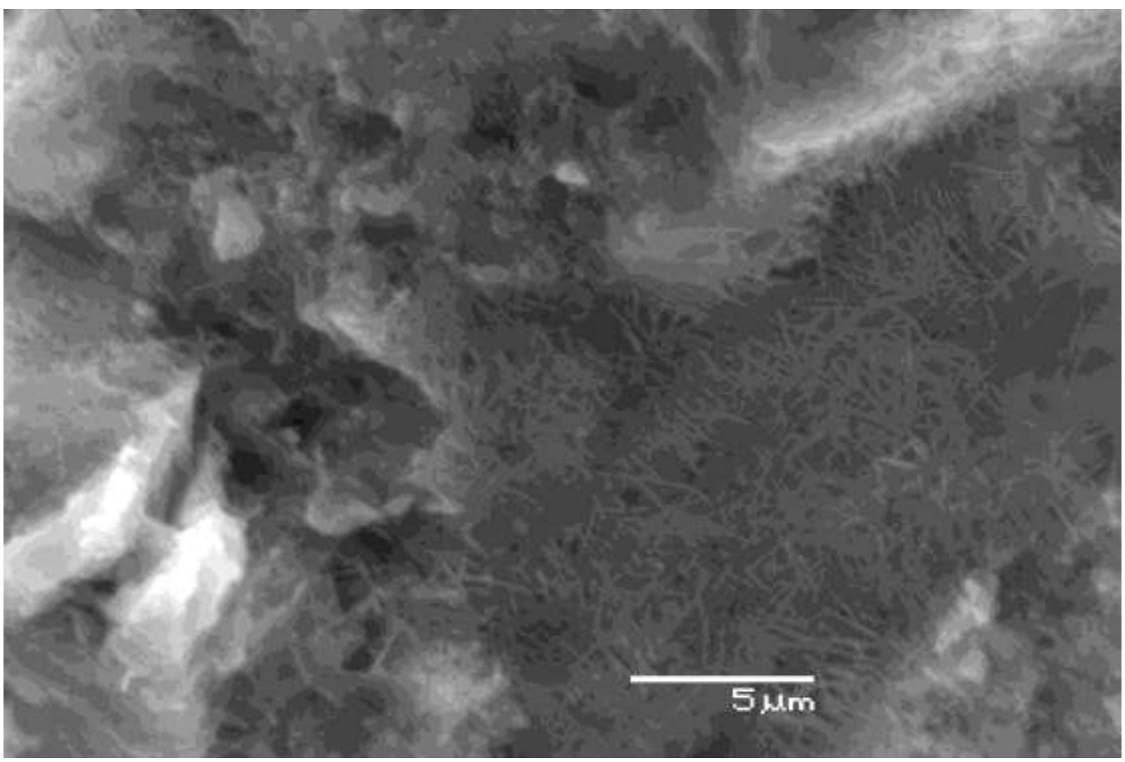

Figure C 3 SEM of 1% Nano clay mixed slurry cured at HPHT for 24 hours

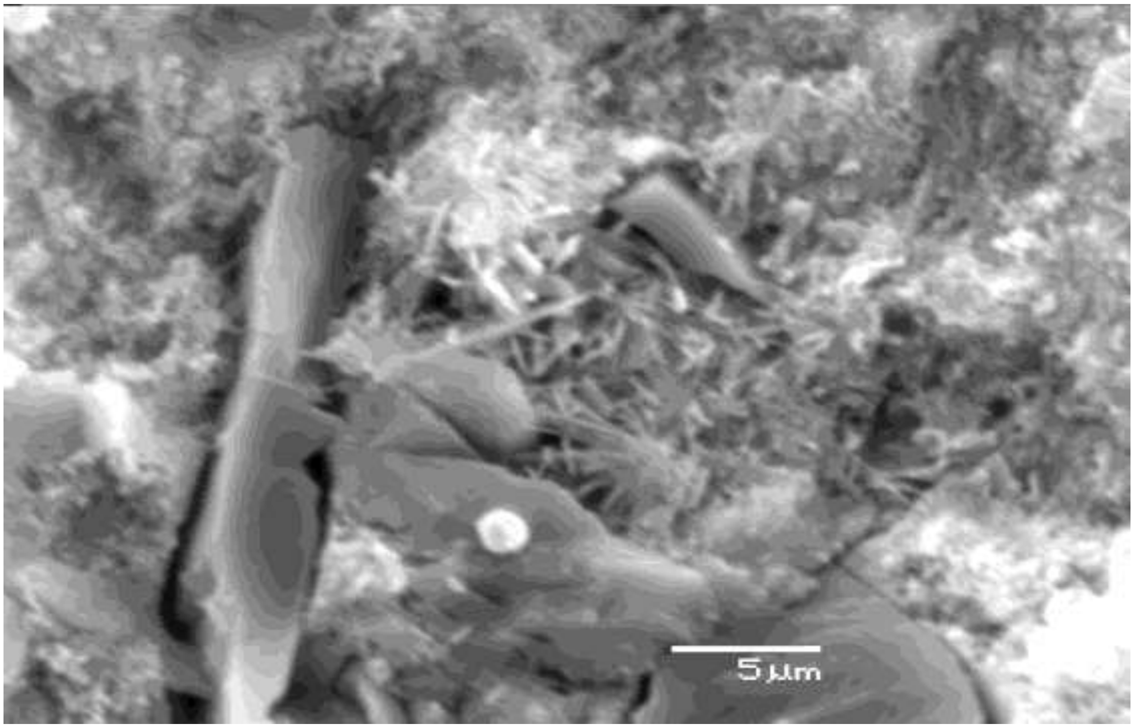

Figure C 4: SEM of 2% Nano clay mixed slurry cured at HPHT for 24 hours

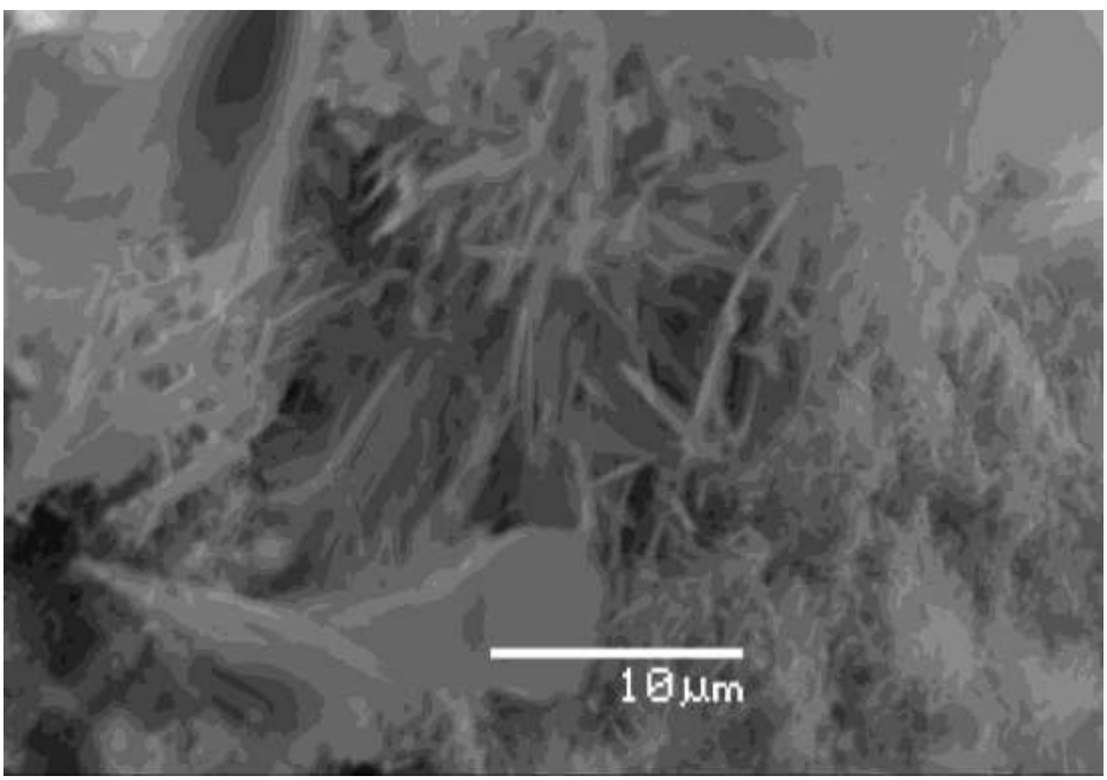

Figure C 5: SEM of 3% Nano clay mixed slurry cured at HPHT for 24 hours

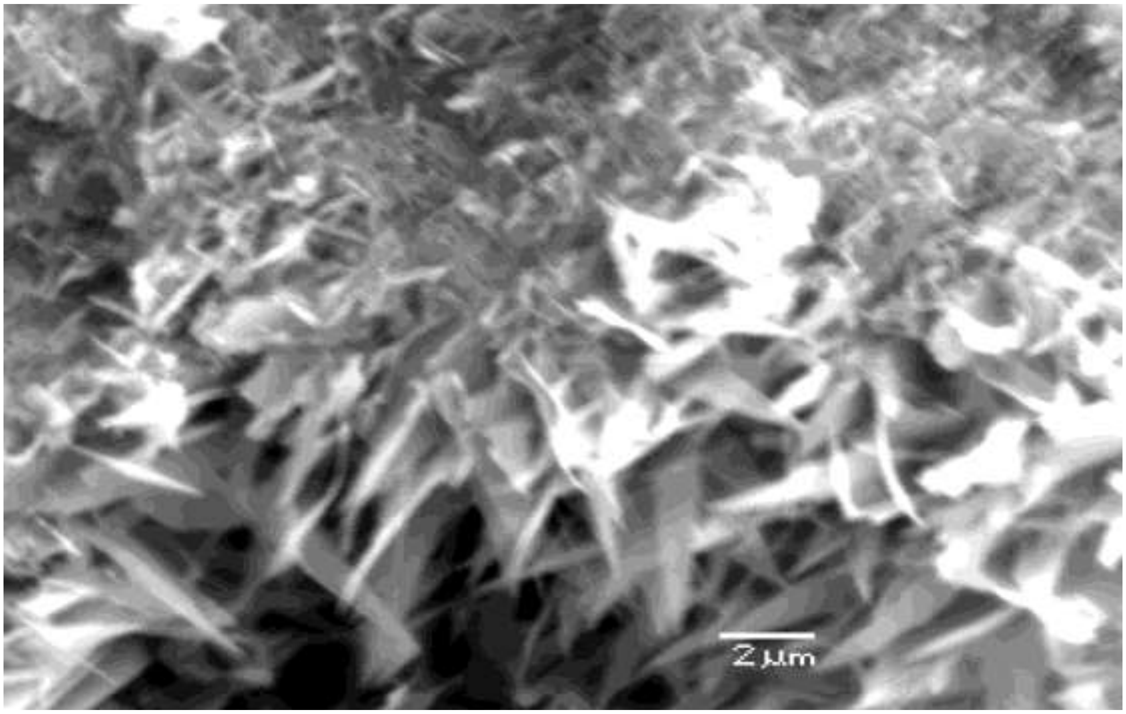

Figure C 6: SEM of 1% Nano silica mixed slurry cured at HPHT for 24 hours

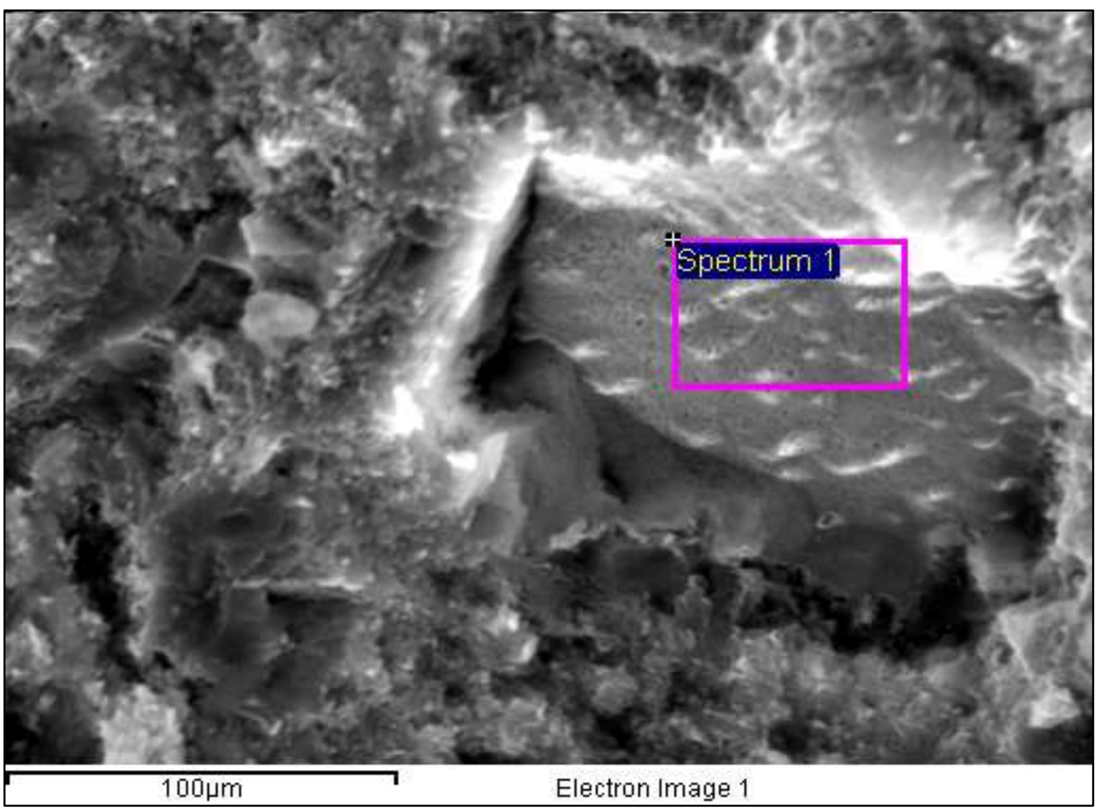

Figure C 7: SEM of 0% Nano clay after curing for 48 hours at HPHT conditions

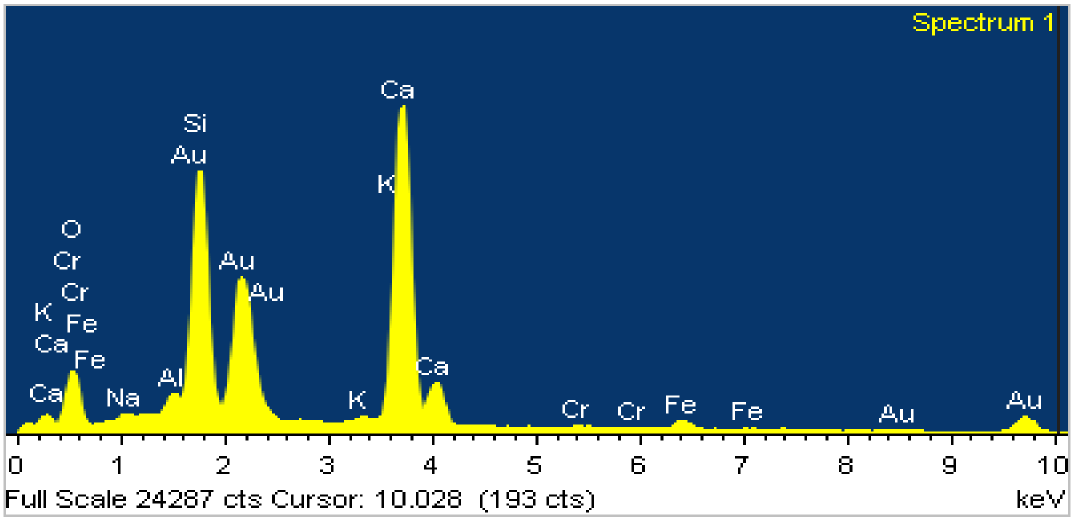

Figure C 8: EDX of 0% Nano clay after curing for 48 hours at HPHT conditions (Spectrum1)

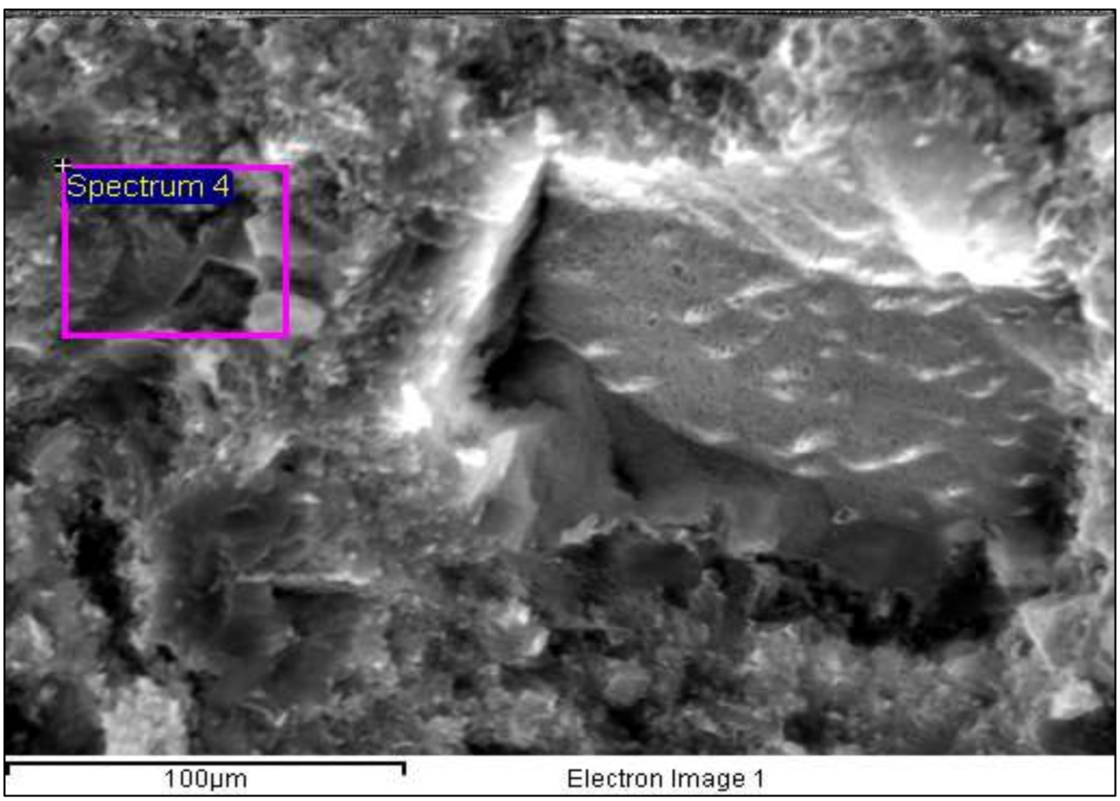

Figure C 9: SEM of 0% Nano clay mixed slurry after curing for 48 hours at HPHT conditions

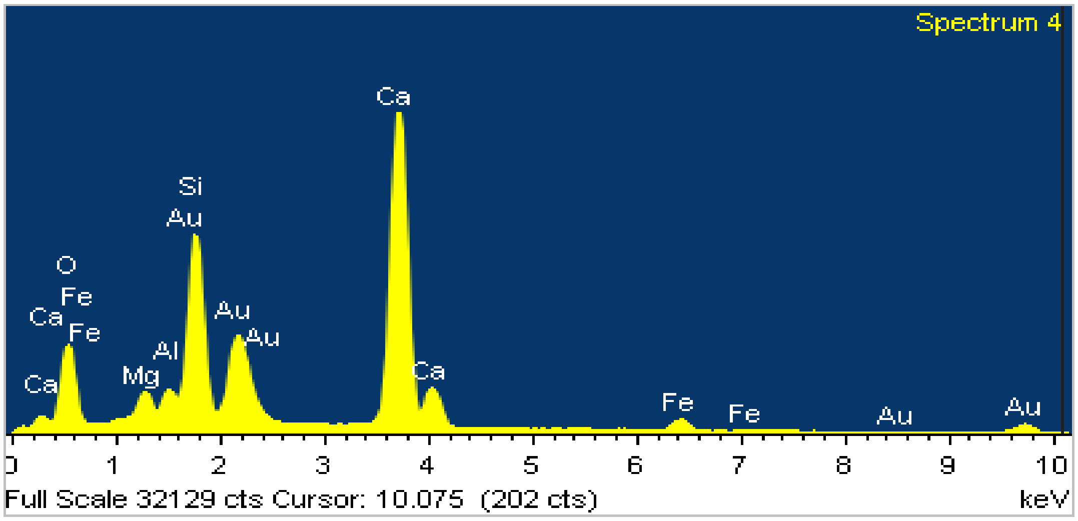

Figure C 10: EDX of 0% Nano clay mixed slurry after curing for 48 hours at HPHT conditions

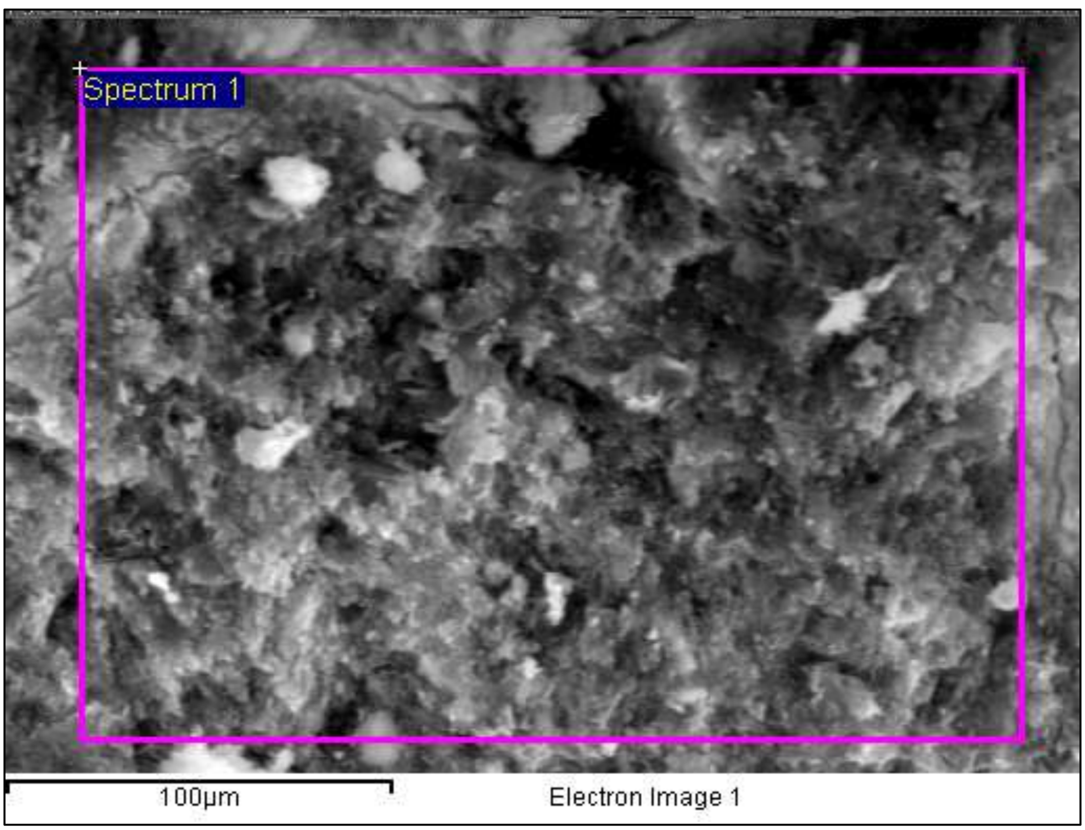

Figure C 11: SEM of 1% Nano clay admixed slurry after curing for 48 hours at HPHT conditions

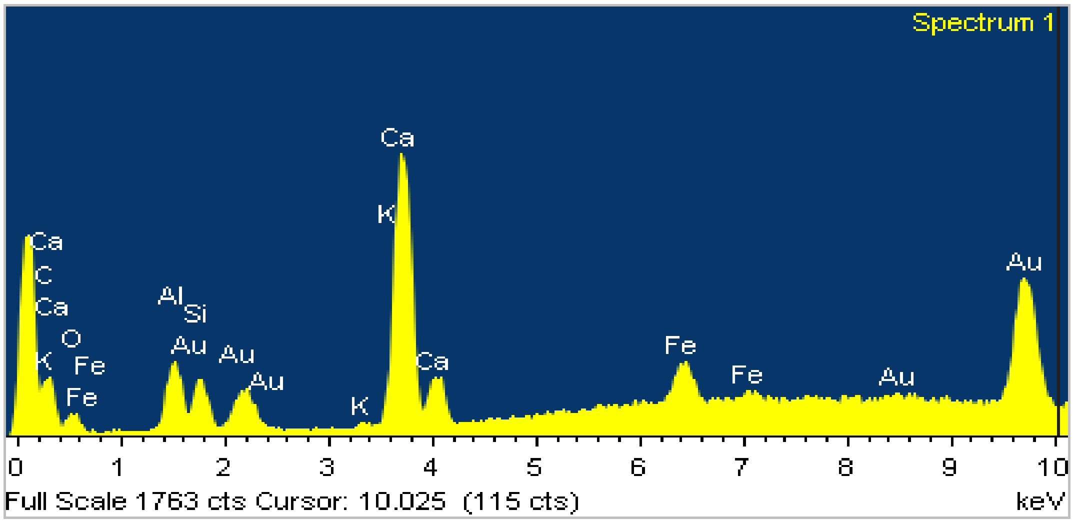

Figure C 12: EDX of 1% Nano clay mixed slurry after curing for 48 hours at HPHT conditions

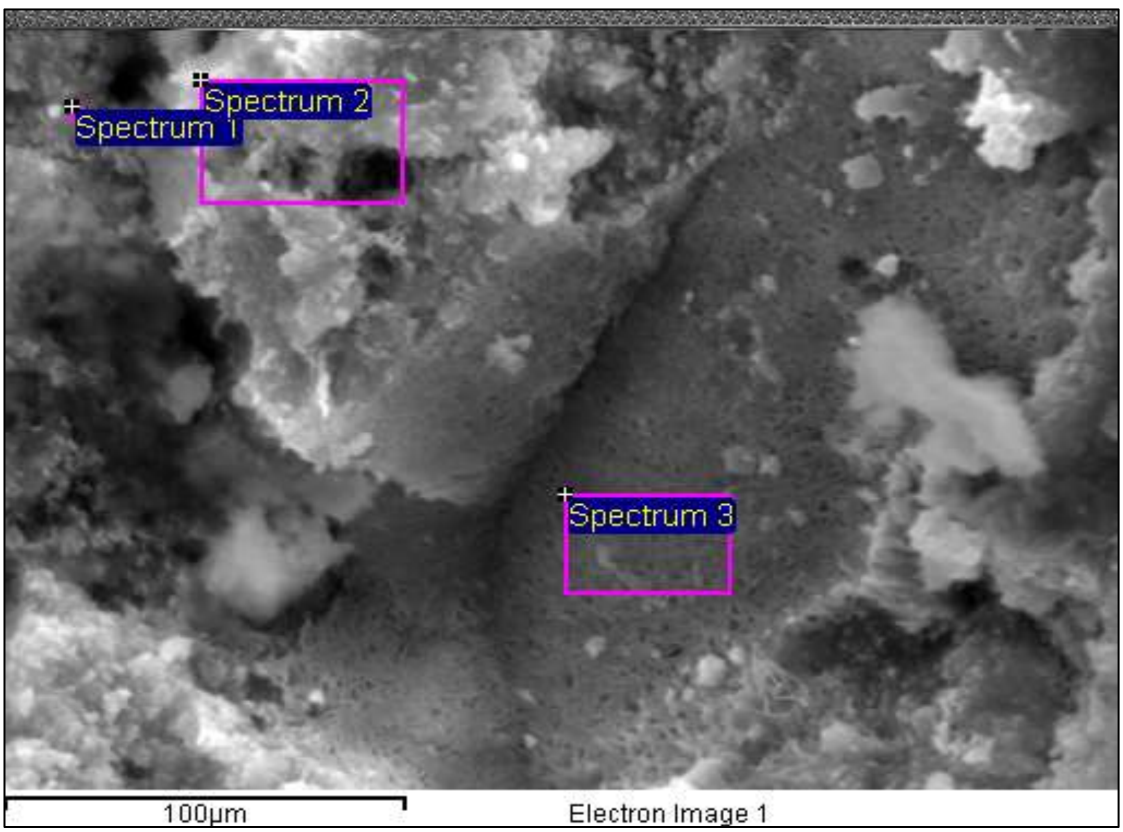

Figure C 13: SEM of 2% Nano clay mixed slurry cured under HPHT conditions for 48 hours

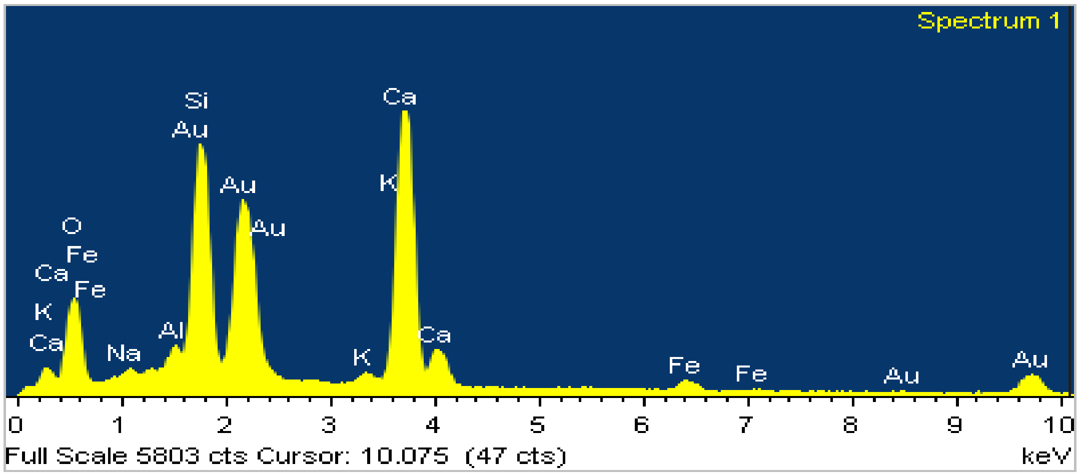

Figure C 14: EDX of 2% Nano clay mixed slurry cured under HPHT conditions for 48 hours (spectrum1)

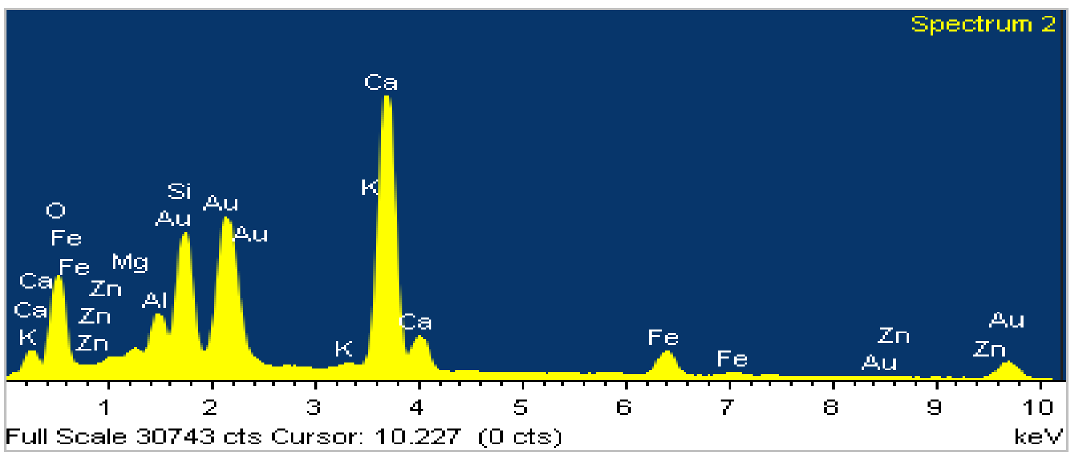

Figure C 15: EDX of 2% Nano clay mixed slurry cured under HPHT conditions for 48 hours (spectrum2)

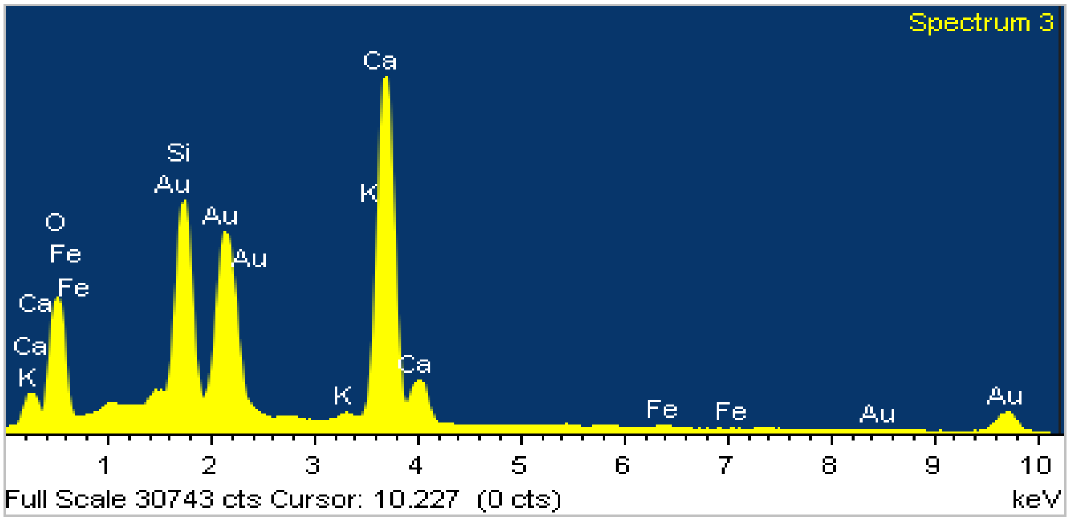

Figure C 16: EDX of 2% Nano clay mixed slurry cured under HPHT conditions for 48 hours (spectrum3)

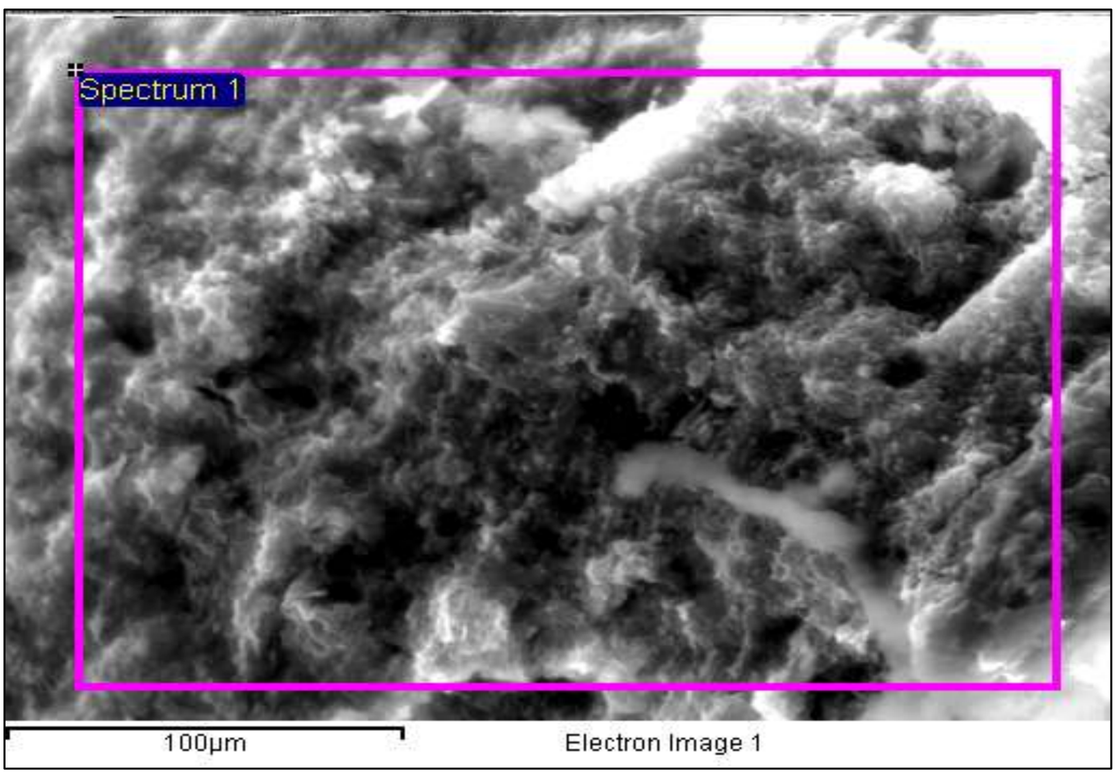

Figure C 17: SEM of 3% Nano clay mixed slurry cured at HPHT for 48 hours

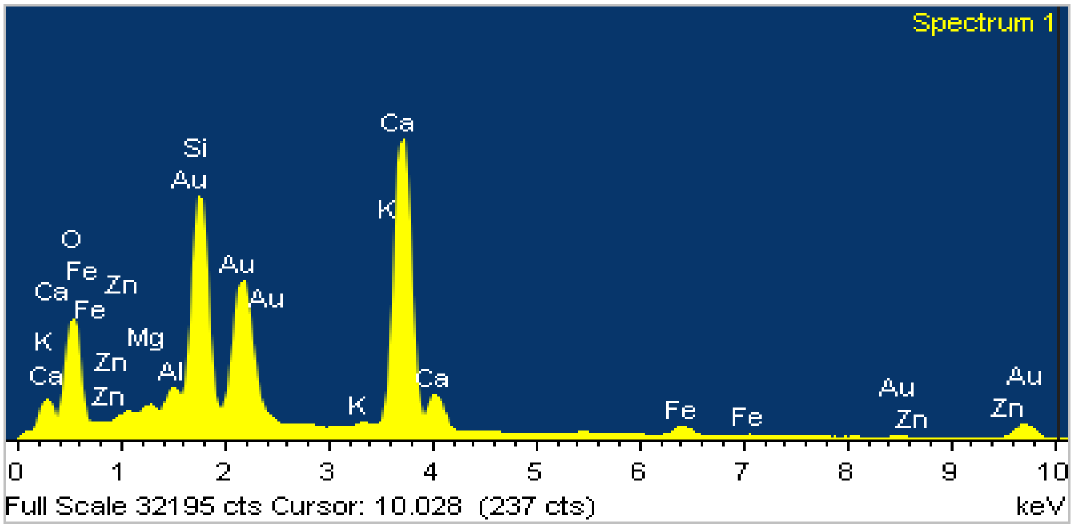

Figure C 18: EDX of 3% Nano clay mixed slurry cured at HPHT for 48 hours (spectrum1)

References

1. A. Martinelli et al. (2004). Accelerating effects of colloidal nano-silica for beneficial calcium–silicate–hydrate formation in cement. *Chemical Physics Letters*, 392(2004), 242–248.
2. Adam T. Bourgoyne et al. (1986). "Applied Drilling Engineering". Ch.3.
3. Ahmed, R. M., Takach, N. E., Khan, U. M., Taoutaou, S., James, S., Saasen, a., & Godoy, R. (2009). Rheology of foamed cement. *Cement and Concrete Research*, 39(4), 353–361.
4. American Petroleum Institute (2012). Specification for Materials and Testing for Well Cements, API Spec.10. USA, Washington DC: American Petroleum Institute.
5. Barnes, H. and Walters (1993). Introduction to Rheology.
6. Beaudoin, J. J., Publishing, W. A., & York, N. (2001). "Handbook of Analytical Techniques in Concrete Science and Technology".
7. Bentz, D.P., Coveney, P.V., Garboczi, E.J. Kleyn, M.F., and Stutzman, P.E. (1994). Cellular automaton simulations of cement hydration and microstructure development. Modelling and Simulation in Materials Science and Engineering. Vol. 2, No. 4, July 1994, pp. 783-808.
8. Bermudez, M. (2007). Effect of sugaron the thickening time of cement slurries. SPE Annual Technical Conference and Exhibition, Anaheim, California, USA, 11-14 November 2007.
9. Berg, W.V. (1979). Influence of specific surface and concentration of solids upon the flow behavior of cement paste. *Magazine of Concrete Research*, Vol. 31, No. 109, pp. 211-216.
10. Billingham, J., Francis, D. T. I., King, a. C., & Harrisson, a. M. (2005). A Multiphase Model for the Early Stages of the Hydration of Retarded Oilwell Cement. *Journal of Engineering Mathematics*, 53(2), 99–112.
11. Buntoro, A., Rubiandini, R., & Key, T. (2001). The effect of neat magnesium oxide (MgO) as expanding additive with burning temperature 1200^{o}C and 1300^{o}C. SPE Annual Technical Conference and Exhibitions Yogyakarta, March 7-10, 2001.
12. Buntoro, A., Yogyakarta, UPN. V. (2000). The effect of neat magnesium oxide (MgO) as expanding additive on cement shear bond strength at high temperature up to 2500^{o}C. World Geothermal Congress Japan, May28- June 10, 2000.
13. Calvert, D.G. Preface. (2006). In: Nelson, E.B. and Guillot, D. (Ed.), Well Cementing, Schlumberger, Texas, 1-11.
14. Campillo, I., Guerrero, a., Dolado, J. S., Porro, a., Ibanez, J. a., & Goni, S. (2007). Improvement of initial mechanical strength by nanoalumina in belite cements. *Materials Letters*, 61(8-9), 1889–1892.
15. Chougnet, A., Audibert, A., Lecolier, E., Moan, M., Guichard, B., Mazard, C., and Valenti, A. (2006). "Polymer Powder/Cement Composites". Proceedings - SPE Annual Technical Conference and Exhibition, 2, San Antonio, Texas, U.S.A., pp. 1176-1183.

16. Coveney, P.V., and Humphries, W. (1996). Molecular modelling of the mechanism of action of phosphonate retarders on hydrating cements. *Journal of the Chemical Society*. Faraday Transactions, Vol. 92, pp. 831 – 841.
17. Carathers, k. and Crook, R. (1987). Surface pipe cement gives high early strength with new cement additives. Proceedings of South-Western Petroleum Short Course, Lubbock, TX, 12-19.
18. Detroit. (1983). "Oil Well Cementing Process".
19. Douglas J.F., Gassiorek J.M. and Swaffield J.A. (1995). “Fluid Mechanics”. Longman Scientific and Technical, Third Edition, ISBN 0582234085, pp. 287-292.
20. Ding, G., Ni, H.J. and Wu, H.W. (2001). Experimental study on action of Latex on cement slurry of oil well. *Journal of the University of Petroleum China*. Vol. 25, No. 2, pp. 16-18.
21. Ershadi, V., Ebadi, T., Rabani, A. R., Ershadi, L., & Soltanian, H. (2011). The effect of Nanosilica on cement matrix permeability in oil well to decrease the pollution of receptive environment. *Internation Journal of Environmental Science and Development*, 128–132.
22. Golapudi, U. K. (1993). Improvement of properties and microstructure of oil-well cements. SPE Journal
23. Guillot, D. (1990). "Rheology of well cement slurries". (Vol. 28, pp. 4–37).
24. Heinold, T., Dillenbeck, R. L., & Company, B. J. S. (2002). The effect of key cement additives on the Mechanical Properties of normal density oil and gas well cement systems. Paper SPE 77867 presented at Asia Pacific Oil and Gas Conference and Exhibition held in Melbourne, Australia 8-10 October, 2012.
25. Yahaba, N. (2010). How does a decrease in oil production affect the world economy. Asia Pacific Economic Papers.
26. Iverson, B., Maxson, J., Bour, D., & Energy, A. (2010). Strength retrogression in cements under high-temperature conditions" Thirty-Fifth Workshop on Geothermal Reservoir Engineering Stanford University, California, February 1-3, 2010 SGP-TR-188.
27. Jalal, M., Mansouri, E., Sharifipour, M., & Pouladkhan, A. R. (2012). Mechanical, rheological, durability and microstructural properties of high performance self-compacting concrete containing SiO_2 micro and nanoparticles. Materials & Design, 34, 389–400.
28. Joel, O. F., & Iseghohi, P. T. (2009). Research and development utilization of local additive in the cementation of HPHT wells in Nigeria . SPE 128608 Annual SPE International Technical Conference and Exhibition in Abeja, Nigeria, 3-5 August, 2009.
29. Jones, R. R. and R. B. Carpenter (1991). New latex, expanding thixotropic cement systems improve job performance and reduce costs”. Paper SPE 21010 presented at SPE International Symposium on Oilfield Chemistry held in Anaheim, California, February 20-22, 1991.
30. Joshi, R.C., and Lohtia, R.P. (Eds.), (1997). Advances in concrete technology, Fly Ash in Concrete: Production, Properties and Uses. Amsterdam, the Netherlands: Gordon and Breach Science Publishers, 269 p.

31. Jupe, A.C., Wilkinson, A.P., Luke, K., and Funkhouser, G.P. (2007). Slurry consistency and In situ synchrotron X-Ray diffraction during the early hydration of Portland cements with calcium chloride. *Journal of the American Ceramic Society*. Vol. 90, No. 8, pp. 2595-2602.
32. Jupe, A. C., Wilkinson, A. P., & Funkhouser, G. P. (2011). Oilwell cement and C_3S hydration under high pressure as seen by In Situ X-Ray diffraction, temperatures ≤80°C with no Additives. *Journal of the American Ceramic Society*, 94(5), 1591–1597.
33. Komonen, J., Penttala, V., & Technology, B. M. (2003). Effects of high temperature on the pore structure and strength of plain and polypropylene fiber reinforced cement pastes.
34. Labibzadeh, M., Zahabizadeh, B., & Khajehdezfuly, A. (2010). Early-age compressive strength assessment of oil well class G cement due to borehole pressure and temperature changes. Journal of the American Science, 6(7), 38–47.
35. Lafarge. Oil Well Cements: Quality And Consistency for over 50 Years, available online at http://www.lafargecorp.com/wps/wcm/resources/file/ebe2760b4c01402/Oil%20Well%20Cements%20-%20PBOWCE.pdf, accessed on 27th September, 2009.
36. Leemann, A., & Winnefeld, F. (2007). The effect of viscosity modifying agents on mortar and concrete. Cement and Concrete Composites, 29(5), 341–349.
37. Li, G. (2004). Properties of high-volume fly ash concrete incorporating nano-SiO_2. *Cement and Concrete Research*, 34(6), 1043–1049.
38. Li, Z., Wang, H., He, S., Lu, Y., & Wang, M. (2006). Investigations on the preparation and mechanical properties of the nano-alumina reinforced cement composite. Materials Letters, 60(3), 356–359.
39. Lu, Y., Guo, X., Huang, Z., Hu, X., and Liu, Y. (2005). Research of polyvinyl alcohol as fluid loss additive of oil well cement. *Natural Gas Industry Journal*. Vol. 25, No.10, pp. 61-63.
40. Kumar, S., Singh, C.J., Singh, R.P. and Kachari, J. (2002). Microfine cement: Special superfine Portland cement. 7th NCB International Seminar, New Delhi, 30th April, 10 pp.
41. Mehta, P. K., & Monteiro, P. J. M. (2001). "Microstructure , Properties and Materials".
42. Michaux, M., & Nelson, E. B. (1990). "Chemistry and Characterization of Portland Cement".
43. Moradi, S., Zonzee, P., Furat, A., Co, P., Sandhu, D., Elarda, H., & Salazar, J. (2006). SPE 101332 Engineered Cement Set Control Additive — Solution for a Long Standing Cementing Challenge.
44. Morsy, M. S., Alsayed, S. H., & Aqel, M. (2012). Effect of Nano-clay on Mechanical Properties and Microstructure of Ordinary Portland Cement Mortar, 23–27.
45. Moulin, E. (n.d.). Using Concrete Technology to Improve the Performance of Lightweight Cements.pdf.
46. Michaux, M., and Defosse, C. (1986). Oil Well Cement Slurries 1. Microstructural Approach of Their Rheology. Cement and Concrete Research, Vol. 16, No. 1, pp. 23-30.

47. Nakayama, M. & J. J. B. (1987). Bond strength development between latex-modified cement paste and steel, 17(c), 562–572.
48. Oilfield Glossary, Weighting Material. Schlumberger Limited, available online at, http://www.glossary.oilfield.slb.com/Display.cfm?Term=weighting%20material, accessed on 24th September, 2009.
49. Park, C. T., & Road, I. (2004). "Nanomaterials – the driving force"..
50. Patil and Deshpande (2012).Use of Nanomaterials in cementing applications. Paper SPE-156937 presented at International Oilfield Nanotechnology Conference held in Noordwijk, The Netherlands, 12-14 June 2012.
51. Popovics, S. (1992). Concrete Materials: Properties, Specifications, and Testing. 2nd edition,Noyes Publication, 661 p.
52. Pourafshary, P., Azimipour, S. S. & Motamedi, P. (2009). Priority assessment of investment in development of Nanotechnology in upstream petroleum industry. Paper SPE 126101 presented at Technical Symposium and Exhibition Saudi Arabia SPE section held in Al Khobar Saudi Arabia, 09-11 May, 2009.
53. Powers, C.A., Holman, G.B., and Smith, R.C. (1977). Process and Composition For Cementing Casing In A Well. United States Patent 4036301.
54. Ramachandran, V.S. (1984). “Concrete Admixtures Handbook: Properties, Science and Technology”. 626 p.
55. Ravi, K.M., and Sutton, D.L. (1990). New Rheological Correlation for Cement Slurries as a Function of Temperature. Paper SPE 20499 was presented at 65th Annual Technical Conference and Exhibition of the Society of Petroleum Engineers, New Orleans, LA, September 23-26, 455-462.
56. Ravi, K and Xenakis, H. (20077). Cementing process optimized to achieve zonal isolation. Halliburton, January 2007
57. Saasen, P. (1991). Experimental investigation of rheology and thickening time of class G oil well cement slurries containing glycerin. Cement and Concrete Research, 911–916.
58. Saidin, S., Sonny, I. & Nuruddin, M. F., (2008). A new approach for optimizing cement design to eliminate microannulus in steam injection wells. Paper IPTC 12407 was presented at the International Petroleum Technology Conference held at Kuala Lumpur, Malaysis, 3-5 December 2008.
59. Santra, A., Boul, P. J., & Pang, X. (2012). Influence of Nanomaterials in oilwell cement hydration and mechanical properties. Paper SPE 156937 was presented at International Oilfield Nanotechnology Conference held in Noordwijk, The Netherlands, 12-14 June 2012.
60. Senff, L., Hotza, D., Repette, W. L., Ferreira, V.M., and Labrincha, J.A. (2009). Influence of added Nano silica and/or silica fume on fresh and hardened properties of mortars and cement pastes. Advances in Applied Ceramics 108 (7): 418–428.
61. Senff, L., Labrincha, J. a, Ferreira, V. M., Hotza, D., & Repette, W. L. (2009). Effect of nano-silica on rheology and fresh properties of cement pastes and mortars. Construction and Building Materials, 23(7), 2487–2491.
62. Shih, J.Y., Chang, T.P., & Hsiao, T.C. (2006). Effect of nanosilica on characterization of Portland cement composite. Materials Science and Engineering: A, 424(1-2), 266–274.

63. Singh, S., & Ahmed, R. (2010). Vital role of Nanopolymers in drilling and stimulations fluid applications. Paper SPE 130413 was presented at Annual Technical Conference held in Flourence, Italy, 19–22 September, 2010.
64. Smith, D.K. (1987). Cementing. Monograph Series, 4, SPE, Dallas, 264 p.
65. Su Z. et al., (1991). The influence of polymer modification on the adhesion of cement pastes to aggregates. Cement and Concrete Research 169–178.
66. Taylor, H.F.W. (1997). Cement Chemistry. London: Academic Press, 475 p.
67. Uddin, F. (2008). Clays, Nanoclays, and Montmorillonite Minerals. *Metallurgical and Materials Transactions* A, 39(12), 2804–2814.
68. US Department of Portland Cement, www.fhwa.dot.gov/infrastructure/materialsgrp/cement.html , 2007.
69. Vlachou, P.V., and Piau, J.M. (1997). The influence of the shear field on the microstrctural and chemical evolution of an oil well cement slurry and its rheological impact. *Cement and Concrete Research*. Vol. 27, No. 6, pp. 869-881.
70. Vidick, B., Fletcher, P., and Michaux, M. (1989). Evolution at early hydration times of the chemical composition of liquid phase of oil-well cement pastes with and without additives. *Cement and Concrete Research*. Vol. 19, No. 4, pp. 567-578, ISSN: 0008-8846.
71. Yetunde, S., & Ogbonna, J. (2011). Challenges and remedy for cementing of HPHT wells in Nigerian operation. Paper SPE 150751 was presented at Annual International Conference and Exhibition held in Nigeria 30 July- 3 August, 2011.
72. Zhang et. al. (2008). Hydration and hardening of class G oilwell cement with and without silica sands under high temperatures. *Journal of the Chinese Ceramic Society*.

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